X. The Bakerian Lecture.—*Chemical Theory of Gunpowder.*
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According to Bellani, the English army used cannon at the Battle of Crecy in the year 1346. The correctness of this report has been doubted since English and French writers in their description of the battle do not mention the use of cannon. However this may be, it is certain, that from the middle of the 14th century the application of powder to the purposes of the art of war became more and more general, until towards the close of the Middle Ages heavy ordnance was used by all European armies. The effect of this new application of gunpowder upon the civilisation of our race is usually considered to have been of the same importance as the invention of the art of printing or the discovery of America. And, although 536 years have passed away since the Battle of Crecy was fought, we have to this day no satisfactory account of the chemical reactions which occur during the combustion of gunpowder, no theory to enable us to determine the quantitative relations of the products of combustion *à priori* from the composition of the powder. The attempts, which have been made from time to time by eminent men to supply solutions of the problems indicated, have been, as is well known, unsuccessful.

In the following pages I propose to describe a theory which explains in a satisfactory manner the chemical reactions which occur during and after the explosion, not only of a powder of normal composition, but, generally, of a mixture of x molecules of saltpetre, y atoms of carbon, and z atoms of sulphur.

Until about the year 1856 the metamorphosis of gunpowder was represented in chemical text-books to take place according to the equation

$$2KNO_3 + 3C + S = K_2S + N_2 + 3CO_2$$
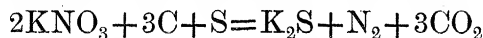
This equation is obviously not correct, because besides sulphide, also sulphate and carbonate of potassium are formed.

After the publication of BUNSEN's and SCHISCHKOFF's[*] classical investigation in 1857, the incorrectness of the equation was generally recognised, and the view expressed that the explosion of gunpowder could not be represented by a chemical equation on account of its complex nature. Passing by for the present the papers published between the years 1858 and 1874, I propose to take at once into consideration the most recent and important investigation by NOBLE and ABEL;[†] I do so because we receive from the pages of their papers a very complete account of our present knowledge of the combustion of gunpowder.

Five different descriptions of powder were used in their experiments.

1. Pebble powder (P.); 2. Rifle large grain (R. L. G.); 3. Rifle fine grain (R. F. G.); 4. Fine grain (F. G.); and 5. Spanish pebble powder.

The first four descriptions were manufactured at Waltham Abbey.

It will be convenient for the purposes of reference to give in the following table the composition of these powders.

TABLE I.—Showing the composition of the powders used by NOBLE and ABEL.

Constituents of powder.	Powders from Waltham Abbey.				Spanish.
	P.	R. L. G.	R. F. G.	F. G.	
Saltpetre	74·67	74·95	75·04	73·55	75·30
Potassic sulphate .	0·09	0·15	0·14	0·36	0·27
Potassic chloride .	..	..	..	..	0·02
Sulphur	10·07	10·27	9·93	10·02	12·42
Charcoal Carbon . . .	12·12 ⎫	10·86 ⎫	10·67 ⎫	11·36 ⎫	8·65 ⎫
Charcoal Hydrogen . .	0·42 ⎬ 14·22	0·42 ⎬ 13·52	0·52 ⎬ 14·09	0·49 ⎬ 14·59	0·38 ⎬ 11·34
Charcoal Oxygen . . .	1·45 ⎪	1·99 ⎪	2·66 ⎪	2·57 ⎪	1·68 ⎪
Charcoal Ash	0·23 ⎭	0·25 ⎭	0·24 ⎭	0·17 ⎭	0·63 ⎭
Water	0·95	1·11	0·80	1·48	0·65

NOBLE and ABEL burnt from 100 to 700 grms. of powder in hermetically closed steel cylinders.[‡] The analyses of the products of combustion obtained in 31 experiments have been published, and of these it will be desirable to reproduce a few representative cases in Table II.

* Pogg. Ann., Bd. cii., p. 321.

† Phil. Trans., Vol. 165 (1875), p. 49, Vol. 171 (1880), p. 203.

‡ Ibid., Vol. 165, p. 61.

TABLE II.—Containing the results of nine experiments calculated for 1 grm.
of powder.

Products of combustion.	F. G.			R. L. G.			P.		
K_2CO_3	0·2429	·2615	·3255	·3007	·3017	·3635	·2879	·3098	·3680
$K_2S_2O_3$	·1851	·1666	·0780	·1166	·0740	·0369	·1845	·0338	·0761
K_2SO_4	·1288	·1268	·1204	·1171	·1395	·0625	·0733	·0658	·0523
K_2S	·0000	·0196	·0252	·0230	·0337	·0565	·0128	·1055	·0220
KCNS	·0009	·0004	·0004	·0000	·0003	·0015	·0022	·0013	·0033
KNO_3	·0010	·0005	·0005	·0032	·0002	·0000	·0014	·0011	·0025
$(NH_4)_4H_2(CO_3)_3$.	·0186	·0002	·0005	·0003	·0002	·0006	·0003	·0004	·0007
S	·0026	·0068	·0306	·0041	·0262	·0480	·0111	·0340	·0484
H_2S	·0090	·0080	·0088	·0041	·0127	·0067	·0129	·0084	·0086
CO	·0316	·0339	·0343	·0303	·0390	·0472	·0419	·0473	·0362
CO_2	·2689	·2678	·2650	·2597	·2610	·2677	·2630	·2770	·2710
CH_4	·0003	·0000	·0005	·0006	·0000	·0007	·0007	·0012	·0013
H	·0006	·0008	·0007	·0005	·0007	·0005	·0005	·0005	·0005
N	·1096	·1071	·1096	·1201	·1108	·1077	·1075	·1139	·1090
No. of experiment	XL.	XIX.	LXXV.	I.	IV.	XXXIX.	XXXVIII.	XIV.	LXXVII.

From this table it is clear that not only powders of different description, but also mixtures of the same nature, will yield during combustion the products in variable quantities. The salts of potassium, especially the hyposulphite and sulphide, vary considerably in different experiments.

NOBLE and ABEL draw the following conclusions from the results of their investigations.

1. "The variations in the composition of the products of explosion furnished in close chambers by one and the same powder, under different conditions as regards pressure, and by two powders of similar composition under the same conditions as regards pressure, are so considerable, that no value whatever can be attached to any attempt to give a general chemical expression to the metamorphosis of a gunpowder of normal composition (p. 137).

"Any attempt to express, even in a comparatively complicated chemical equation, the nature of the metamorphosis which a gunpowder of average composition may be considered to undergo when exploded in a confined space, would therefore only be calculated to convey an erroneous impression as to the simplicity or the definite nature of the chemical results and their uniformity under different conditions, while it would, in reality, possess no important bearing upon an elucidation of the theory of explosion of gunpowder (p. 85).

2. "The proportions in which the several constituents of solid powder-residue are formed, are quite as much affected by slight accidental variations in the conditions which attend the explosion of one and the same powder in different experiments, as

by decided differences in the composition as well as in the size of grain of different powders (p. 137).

3. "Very small grain powder, such as F. G. and R. F. G. furnish decidedly smaller proportions of gaseous products than a large grain powder (R. L. G.), while the latter again furnishes somewhat smaller proportions than a still larger powder (pebble), though the difference between the gaseous products of these two powders is comparatively inconsiderable.

4. " In all but very exceptional results, the solid residue furnished by the explosion of gunpowder contains as important constituents, potassium carbonate, sulphate, hyposulphite and sulphide, the proportion of carbonate being very much higher, and that of sulphate very much lower than stated by recent investigators."

The view of NOBLE and ABEL may be briefly stated as follows :—

One and the same description of powder, exploded several times in succession, will yield the products of combustion, in the different experiments, in variable proportions; hence: the metamorphosis of gunpowder cannot be represented by a chemical equation.

One might suppose that, perhaps, the pressure developed during explosion had an influence on the quantities of the products of combustion. From a comparison of the analytical results and the corresponding pressures, published by NOBLE and ABEL, this, however, appears not to be the case.* (See p. 85 of their first memoir.)

According to NOBLE and ABEL, the chemical metamorphosis of gunpowder during explosion is a very complicated process, which cannot be explained with the data at their disposal. BERTHELOT † arrived at a different conclusion.

The composition of the powders of Waltham Abbey can, according to him, be represented by the symbols

$$2KNO_3 + 3C + S$$
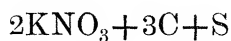
which require for 100 parts of powder :

Saltpetre	74·8
Carbon	13·3
Sulphur	11·8

The analyses gave :

Saltpetre	73·55 to	75·04
Carbon	10·67	12·12
Sulphur	9·93	10·27

* An increase of pressure appears to diminish the amount of carbonic oxide. But this is not always the case, and when it does occur, it is not sufficient to explain the variations in the other products of combustion.
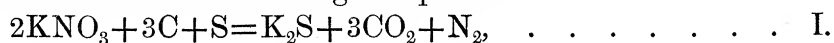
† Comptes Rendus, tom. lxxxii., p. 487.

The combined weights of potassic sulphocyanate, ammonic carbonate, hydrogen, marsh gas, and sulphuretted hydrogen amount, according to Table II., to about 1·5 per cent. They evidently originate from secondary reactions, and may, accordingly, be neglected in the following considerations.
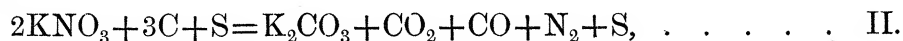
A theory of the explosion of gunpowder ought to explain the formation of potassic carbonate, potassic sulphate, potassic sulphide, carbonic acid and carbonic oxide. Potassic hyposulphite is not a primary product, but is formed during the analysis of the powder residue.

If we select two from several experiments published by NOBLE and ABEL, viz. :— one in which the maximum amount of potassic carbonate and the minimum of sulphate were produced, and another which yielded the largest quantity of potassic sulphate and the smallest of carbonate, then, according to M. BERTHELOT, the explosion which produced the results of the first case, may be represented by three equations—
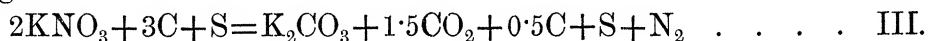
$\frac{1}{3}$ of the powder was transformed according to equation
$$2KNO_3 + 3C + S = K_2S + 3CO_2 + N_2, \qquad \text{I.}$$
$\frac{1}{2}$ according to
$$2KNO_3 + 3C + S = K_2CO_3 + CO_2 + CO + N_2 + S, \qquad \text{II.}$$
$\frac{1}{6}$ according to
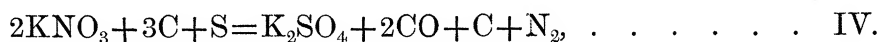$$2KNO_3 + 3C + S = K_2CO_3 + 1·5CO_2 + 0·5C + S + N_2 \qquad \text{III.}$$

and in the second case, with a maximum of potassic sulphate,

$\frac{1}{3}$ of the powder was transformed according to equation I,
about $\frac{1}{2}$ according to III,
$\frac{1}{8}$ according to
$$2KNO_3 + 3C + S = K_2SO_4 + 2CO + C + N_2, \qquad \text{IV.}$$
and $\frac{1}{12}$ according to
$$2KNO_3 + 3C + S = K_2SO_4 + CO_2 + C_2 + N_2 \qquad \text{V.}$$
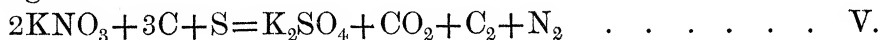
Between the limits, marked by these two cases, are contained all the experimental results of NOBLE and ABEL. If, therefore, we assume that in a given experiment one portion of the powder used burnt according to the equations of the first, and the rest according to those of the second case, the calculated results will agree with the observations. And if the proportions of powder, which are transformed according to the one or other system of equations, be changed from experiment to experiment, the quantities of the products of combustion obtained in each experiment can be calculated in a satisfactory manner.

The assumption that during explosion one portion of the powder is transformed according to one and another portion according to another equation or system of equations is justified in the opinion of M. BERTHELOT by the further assumption, that the local conditions in a mass of burning powder are not the same in all parts, and that the cooling is too rapid to allow the products to assume a state of chemical equilibrium.

If the products were left in contact at a high temperature for a longer time, they would react upon each other, and the final result would be the same as that represented by equation V., to which corresponds the greatest evolution of heat.

This theory of M. BERTHELOT is very ingenious, but does not agree with experience. Considerable amounts of carbon ought to be left free at the end of each explosion. In 28 experiments of NOBLE and ABEL no free carbon was left, and only in three cases small insignificant quantities had escaped combustion. The equations III., IV. and V. cannot be applied to the combustion of the powders of Waltham Abbey. But even if the theory were correct, it would possess no practical value, because the quantities of the powder which would burn according to each of the two systems of equations, could not be known *à priori*, but would have to be found by experiment.

BERTHELOT invented his theory in order to explain the remarkable result of NOBLE and ABEL's experiments, that the same description of powder, or powders of similar composition, yield the products of explosion, in different experiments, in variable proportions.

We will now proceed to show that this result can be explained, without hypothesis or theory, in a very simple manner.

For this purpose it is desirable to express the analytical results of NOBLE and ABEL in a manner different from the one adopted by these investigators.* If we divide the numbers of Table II. by the corresponding molecular weights, we obtain another table expressing the number of molecules of the products obtained in the different experiments by the explosion of 1 grm. of powder. For Experiment XIX. we have :—

K_2CO_3	0·2615 gramme or	0·00189 mol.
K_2SO_4	0·1268 ,,	0·00072 ,,
$K_2S_2O_3$	0·1666 ,,	0·00087 ,,
K_2S_2	0·0252 ,,	0·00017 ,,
S	0·0012 ,,	0·00004 atom.
CO_2	0·2678 ,,	0·00608 mol.
CO	0·0339 ,,	0·00121 ,,
N	0·1071 ,,	0·00765 atom.
H_2S	0·0080 ,,	0·00023 mol.
CH_4	0·0000 ,,	0·00000 ,,
H	0·0008 ,,	0·00080 atom.
KCNS	0·0004 ,,	
KNO_3	0·0005 ,,	
$Am_4H_2(CO_3)_3$ . .	0·0002 ,,	

Potassic carbonate, sulphate, sulphide, and hyposulphite, carbonic acid and carbonic

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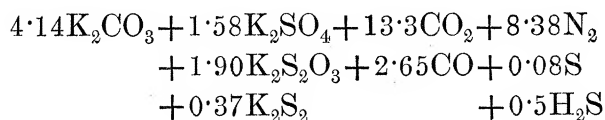* NOBLE and ABEL discuss only the percentage quantities of the products of explosion.

oxide, nitrogen and sulphuretted hydrogen together form more than 98 per cent. of the exploded powder; accordingly, hydrogen, marsh gas, ammonic carbonate, potassic sulphocyanate and undecomposed saltpetre may, as non-essential products, be left out of consideration.

Potassic carbonate, sulphate, hyposulphite, and sulphide contain very nearly the entire amount of potassium of the exploded powder. If, therefore, we add the number of molecules of these bodies and multiply the sum by two, we obtain the number of molecules of saltpetre in 1 grm. of powder. In order to compare the results of experiments made with the same or with different descriptions of gunpowder it is desirable to calculate these results, not, as is usually done, for the same quantity of powder, but for such quantities as contain equal amounts of saltpetre or oxygen.

The products of Experiment XIX. contain 0·00730 atom of potassium and are derived from a weight of powder containing 0·0073 mol. of saltpetre. The same products contain 0·00189 mol. of K_2CO_3, hence :

$$0·00730 : 0·00189 :: 16 : x \text{ and } x = 4·14.$$

And if the same mode of calculation is extended to the other products, we obtain

$$4·14K_2CO_3 + 1·58K_2SO_4 + 13·3CO_2 + 8·38N_2$$
$$+ 1·90K_2S_2O_3 + 2·65CO + 0·08S$$
$$+ 0·37K_2S_2 \qquad\quad + 0·5H_2S$$

and, from these numbers, the following composition of the F. G. powder,

$$16KNO_3 + 20·09C + 6·70S$$
$$+ 0·76N + 1·0H$$
$$+ 5·69O.$$
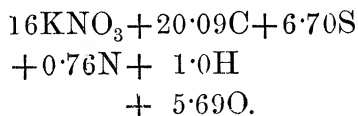
By a similar calculation we obtain :

Experiment LXXV.

$$\left.\begin{array}{l} 5·10K_2CO_3 + 13·08CO_2 + 0·56H_2S \\ 1·50K_2SO_4 + 2·65CO \\ 0·89K_2S_2O_3 + 8·5N_2 \\ 0·48K_2S_2 + 1·58S \end{array}\right\} = \left\{\begin{array}{l} 16KNO_3 + 20·83C \\ 0·5N_2 + 6·38S \\ 4·78O \\ 1·12H \end{array}\right.$$

Experiment IV.

$$\left.\begin{array}{l} 4·75K_2CO_3 + 12·92CO_2 + 0·80H_2S \\ 1·74K_2SO_4 + 3·03CO \\ 0·85K_2S_2O_3 + 8·6N_2 + 1·11S \\ 0·65K_2S_2 \end{array}\right\} = \left\{\begin{array}{l} 16KNO_3 + 20·7C \\ 6·65S + 0·6N_2 \\ + 1·60H \\ + 4·63O \end{array}\right.$$

Experiment XXXIX.

$$\left. \begin{array}{l} 5\cdot70K_2CO_3 +13\cdot18CO_2+0\cdot41H_2S \\ +0\cdot78K_2SO_4 + 3\cdot64CO \\ +0\cdot41K_2S_2O_3+ 8\cdot3N_2 \quad +2\cdot14S \\ +1\cdot10K_2S_2 \end{array} \right\} = \left\{ \begin{array}{l} 16KNO_3+22\cdot52C \\ +6\cdot35S +0\cdot3N_2 \\ +0\cdot82H \\ +3\cdot45O \end{array} \right.$$

Experiment XIV.

$$\left. \begin{array}{l} 4\cdot77K_2CO_3 +13\cdot44CO_2+0\cdot51H_2S \\ +0\cdot79K_2SO_4 + 3\cdot62CO \\ +0\cdot36K_2S_2O_3+ 8\cdot67N_2 \quad +0\cdot21S \\ +2\cdot04K_2S_2 \end{array} \right\} = \left\{ \begin{array}{l} 16KNO_3+21\cdot83C \\ +6\cdot31S +0\cdot67N_2 \\ +1\cdot02H \\ +1\cdot05O \end{array} \right.$$

Experiment LXXVII.

$$\left. \begin{array}{l} 5\cdot95K_2CO_3 +13\cdot78CO_2+0\cdot55H_2S \\ +0\cdot67K_2SO_4 + 2\cdot88CO \\ +0\cdot89K_2S_2O_3+ 8\cdot7N_2 \quad +2\cdot93S \\ +0\cdot44K_2S_2 \end{array} \right\} = \left\{ \begin{array}{l} 16KNO_3+22\cdot61C \\ +6\cdot81S + 0\cdot7N_2 \\ +1\cdot10H \\ +5\cdot64O \end{array} \right.$$

These equations represent only the quantitative relations between the constituents of the powders and the products of explosion, and, accordingly, fractions of atoms and molecules are admissible.

Experiments XIX. and LXXV. were made with F. G., Experiments IV. and XXXIX. with R. L. G., and Experiments XIV. and LXXVII. with P. powder of Waltham Abbey.

It will be noticed by comparing two experiments, made with the same description of powder, that the composition of the powder deduced from one of the experiments exhibits considerable differences from the composition derived from the other experiment, and neither of them agrees with the composition found by direct analysis.

The composition of the R. L. G. powder may serve as an example.

According to Experiment IV. . . $16KNO_3+20\cdot7C +6\cdot65S+4\cdot63O$
    „   „ Experiment XXXIX. $16KNO_3+22\cdot52C+6\cdot35S+3\cdot45O$
    „   „ Analysis of powder . $16KNO_3+19\cdot51C+6\cdot92S$

The products of combustion of Experiment IV. contain 1·2, and of Experiment XXXIX. 3 atoms more carbon than the powder used in these experiments, or in other words : the products of explosion in Experiment XXXIX. were found to contain 1·67 per cent. more carbon than the R. L. G. powder which was exploded.

The results of other experiments, made by NOBLE and ABEL, differ from each other in a similar manner.

One is forced to conclude either that the methods of analysis adopted by NOBLE and ABEL do not yield exact results, or that the powders exploded did not possess the composition which was attributed to them.

Gunpowder is a mechanical mixture of saltpetre, charcoal, and sulphur. It can hardly be expected that such a mixture should, even if the greatest care has been taken by the manufacturer, be perfectly homogeneous. Moreover, the burning of wood into charcoal will not always yield a product containing the same percentage amount of carbon, and as gunpowder is a mixture of 75 parts of saltpetre, 10 of sulphur, and 15 of charcoal, it appears à priori probable that the same description of powder from the same manufacturer will not always possess the same percentage composition. The amount of carbon, more particularly, may be expected to vary more or less.

In order to test this conclusion by experiment, I requested the late Mr. WILLS to analyse a sample of R. L. G. and one of pebble (P.) powder, both obtained from the Royal Arsenal, Woolwich. His results, placed side by side with those of NOBLE and ABEL, are given below.

	R. L. G.		P.	
	NOBLE and ABEL.	WILLS.	NOBLE and ABEL.	WILLS.
Saltpetre	74·95	75·10	74·67	74·26
Sulphur	10·27	8·96	10·07	9·51
Charcoal—				
Carbon . . .	10·86	12·09	12·12	11·58
Hydrogen. . .	0·42	0·54	0·42	0·51
Oxygen . . .	1·99	2·12	1·45	2·55
Ash.	0·25	0·20	0·23	0·33
Water	1·11	0·85	0·95	0·76
	99·85	99·86	99·91	99·50

It will be noticed that the amounts of carbon and sulphur found by WILLS differ considerably from those found by NOBLE and ABEL. But the best proof that the same description of powder from the same works may vary much in composition has been furnished by NOBLE and ABEL themselves. In their first memoir they assign to R. L. G. powder the above composition; in their second paper "On Fired Gunpowder" they publish the following analysis :—

$$
\begin{array}{lr}
\text{Saltpetre.} & 74\cdot43 \\
\text{Sulphur} & 10\cdot09 \\
\text{Charcoal—} & \\
\quad\text{Carbon} & 12\cdot40 \\
\quad\text{Hydrogen} & 0\cdot40 \\
\quad\text{Oxygen} & 1\cdot27 \\
\quad\text{Ash} & 0\cdot21 \\
\text{Water} & 1\cdot05 \\
\hline
& 99\cdot85
\end{array}
$$

The sample used in the first analysis was taken from the top, the one employed in the second from the bottom of the same barrel. Two analyses of powder out of the same barrel, executed by the same chemists, gave amounts of carbon which differ from each other by no less than 1·54 per cent.! We will now consider the effect of such a difference in the percentage of carbon on the relative quantities of the products of combustion.

If in one experiment 100 grms. of powder containing 75 parts of saltpetre, 10 parts of sulphur, and 10·86 parts of carbon, and in a second experiment 100 grms. of powder with 74·43 parts of saltpetre, 9 parts of sulphur, and 12·40 parts of carbon had been exploded, then, *cæteris paribus*, in the second experiment more potassic carbonate, more sulphide and less sulphate must have formed than in the first, and the quantitative differences of the same products furnished by the two experiments would be almost as great as the greatest differences actually observed by NOBLE and ABEL for the same description of powder in the whole series of their experiments. We arrive in this manner at a very simple explanation of the experimental results upon which NOBLE and ABEL have based the conclusions mentioned under No. 1 and 2 on p. 525, without the necessity of having recourse to a theory like the one advanced by M. BERTHELOT, or renouncing all explanation like NOBLE and ABEL.

It follows from Table I. that the differences of composition between P., R. L. G., R. F. G., and F. G. powders, one compared with the other, are not greater than the differences between two samples of R. L. G. powder taken out of the same barrel. From this it appears probable that only one mixture of saltpetre, charcoal, and sulphur is prepared at Waltham Abbey, and that from this one mixture the powders P., R. L. G., R. F. G., and F. G., differing only in size of grain and, perhaps, density, are manufactured. We may take then for the composition of the said powders the mean of the numbers of all published analyses. Taking into consideration only the saltpetre, sulphur, and carbon, we obtain—

R. L. G. First analysis by NOBLE and ABEL . . $16KNO_3+19\cdot51C+6\cdot92S$
   ,,   Second   ,,   ,,   . . $16KNO_3+22\cdot40C+6\cdot83S$
F. G. . . . . $16KNO_3+20\cdot8C+6\cdot8S$
P.. . . . . $16KNO_3+21\cdot86C+6\cdot79S$

and for the mean $16KNO_3+21\cdot14C+6\cdot83S$.

If also the analyses of the late Mr. WILLS are taken into consideration, then the mean composition of the powders of Waltham Abbey would be represented by the symbols

$$16KNO_3+21\cdot18C+6\cdot63S$$
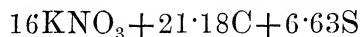
The differences of composition found by analysis for the same description of powder are also of great importance in the calculations of the analytical results of the products of explosion. NOBLE and ABEL determine the potassium in x parts of the solid powder residue, and by means of the number so obtained calculate the weight of the total residue. The amount of potassium in the quantity of powder exploded is known from the analysis of the powder, and as the whole of this potassium must reappear in the solid residue, it is easy to find the total residue if the weight of potassium in x parts of it are known.

The total weight of the powder residue subtracted from the weight of the powder used in the experiment gives as difference the total weight of the gases produced by the explosion.

This mode of calculation requires that the exact composition of the powder used in each experiment should be known. Messrs. NOBLE and ABEL assume the composition of the powders of Waltham Abbey, P., R. F. G., and F. G., to be constant; they also consider in their first memoir that of R. L. G. to be so, but in their second memoir they base the calculations of the later experiments on the second analysis of this description of powder. This assumption is, as a matter of fact, not correct; on the contrary, we may take it as highly probable, that in any two experiments made by NOBLE and ABEL with the same class of powder, the powder used in the one experiment was not exactly of the same composition as the powder used in the other. Accordingly the weight of the solid residue as calculated by NOBLE and ABEL will have been found in some experiments too high, in others too low, and as a consequence of this the total weight of the gaseous products cannot have been exact. The correctness of this is proved by the differences between the composition of the powders calculated from the products of combustion, and the composition deduced from direct analysis (see pp. 530, 531). These errors will, however, compensate each other if we take the mean of the analytical results of all the experiments.

Before we proceed to do so it will be desirable to consider another circumstance which is not without influence on the final results of Messrs. NOBLE and ABEL.

They burnt their powders in steel cylinders in quantities from 100 to 750 grms., so that the solid products of combustion after explosion remained from 60 to 120 seconds

in contact in a fluid condition at a high temperature. Amongst these products we have not, as is usually assumed, potassium monosulphide, but disulphide, free sulphur, and potassium carbonate. But a mixture of polysulphides of potassium and potassium carbonate at a bright red or a white heat has a most powerful corroding effect upon metals. It is well known that the celebrated STAHL was of opinion that MOSES had dissolved the golden calf of the Israelites by means of a polysulphide of potassium.

"And he took the calf which they had made, and burnt it in the fire, and ground it to powder and strewed it upon the water, and made the children of Israel drink of it." —(Exod. xxxii. 20.)

Sulphur and ash of wood were known to the Jews, and these, at a high temperature, form liver of sulphur, capable of dissolving gold. The affinity of iron for sulphur is very strong. We may expect that, according to temperature, pressure, time of cooling, and last but not least, the condition of the surface of the cylinder, more or less of the sulphur of the powder would unite with the iron of the apparatus. This would have the same effect upon the products as if a powder with less sulphur had been burnt. If 400 grms. of powder of the average composition had been exploded, and 10 grms. of its sulphur were to unite with the iron of the apparatus, the potassium carbonate produced would be about 0·20 time greater than the amount obtained by the combustion of the same quantity of powder without this removal of sulphur by the iron of the apparatus.

According to the description given by NOBLE and ABEL of the solid powder residue, considerable quantities of ferrous sulphide were contained in it. Hence the variations in the quantities of the products of combustion of powders exploded in NOBLE and ABEL's apparatus will partly be due to the chemical action of iron and sulphur at high temperatures.

It will be observed by an inspection of the equations on pages 529 and 530, that considerably more oxygen was found in the products of combustion than was contained in the saltpetre of the exploded powder. This excess of oxygen cannot have been derived from the charcoal, or the moisture of the powder, because if it had, equivalent quantities of hydrogen ought to have been liberated. Charcoal contains more hydrogen than is necessary to form water with its oxygen. It is this excess of hydrogen which is set free, or which unites with sulphur, carbon or nitrogen forming sulphuretted hydrogen, marsh gas, or ammonia.

Hence, the excess of oxygen in the products of explosion must originate from some other source. NOBLE and ABEL, like LINCK, KAROLYI and others, adopted the method proposed by BUNSEN and SCHISCHKOFF for the analysis of the solid powder residue. This method requires that the aqueous solution of the substance should be digested with cupric oxide in order to convert the potassic sulphide into hydrate. The question suggested itself whether or not oxygen from the cupric oxide had formed with potassic sulphide, sulphate or hyposulphite.

27·3 grms. pure potassic hydrate were dissolved in water, which previously had been

boiled in order to expell the air, and the solution divided into two equal parts. One of these parts was saturated with sulphuretted hydrogen in an atmosphere of hydrogen and then mixed with the other, and the solution of potassic sulphide, so obtained, digested with powder of sulphur in sufficient quantity to produce pentasulphide. The analysis of this liquid gave the following results :—

10 cub. centims. diluted with previously boiled water were acidulated with hydric chloride and heated to the boiling point. A precipitate of 1·094 grms. of sulphur was obtained. The filtrate evaporated to dryness and ignited, the dry residue moistened with hydric chloride, and then raised to a red heat gave 1·387 grms. of potassic chloride, corresponding to 0·726 grm. of potassium. On the assumption that 1 atom of sulphur had escaped as sulphuretted hydrogen, the liquid, according to these determinations, contains sulphur and potassium in the proportion of 4·67 atoms of the former to 2 atoms of the latter.

10 cub. centims. of the sulphide mixed with a solution of zinc sulphate, and the filtrate tested with an iodine solution in presence of some starch required 0·2 cub. centim. of the iodine liquid in order to produce a blue colour. 1 cub. centim. of the iodine solution corresponded to 1 cub. centim. of a solution of sodium hyposulphite containing 24·8 grms. of the salt in 1 litre.

Therefore, 10 cub. centims. of the polysulphide of potassium contain :

> 0·0038 grm. potassic hyposulphite
> 2·119 grms. potassic polysulphide.

To check these numbers, Mr. COWPER at my request dissolved the zinc sulphide in hydric nitrate of 1·5 sp. grav., and determined the zinc and the sulphur in the solution according to the usual methods.

He obtained :

> Sulphur . . . . 1·285 grms.
> Zinc. . . . . . 0·556 grm.

or for every atom of zinc 4·69 atoms of sulphur.

180 cub. centims. of the solution of potassic polysulphide were digested in a hermetically closed flask with pure and previously ignited cupric oxide at common temperatures. The liquid assumed a brown colour, which still could be observed after two days' digestion. The flask was now placed in water of 35° C., whereupon the colour rapidly disappeared. The contents of the flask were now placed upon a filter, the cupric oxide and sulphide well washed, and filtrate and wash water united and kept in a closed bottle.

I. 25 cub. centims. of the liquid so prepared, neutralised with acetic acid, mixed with some starch solution, required 24·6 cub. centims. of iodine solution for the production of the blue colour.

25 cub. centims. in another experiment required 24 cub. centims. iodine solution.

25 cub. centims. in a third experiment required 24·2 cub. centims. iodine solution.

The mean of these experiments is 24·26 cub. centims. of iodine solution for 25 cub. centims. of the filtrate, hence, 100 cub. centims. of the united filtrate and wash water contain 1·844 grms. of potassic hyposulphite.

II. 100 cub. centims. of the same filtrate evaporated with pure hydric sulphate gave 3·653 grms. of potassic sulphate, which dissolved in water to a clear and neutral liquid. A similar quantity of hydric sulphate to that which had been used in this experiment, and out of the same bottle, left no residue after evaporation. 3·653 grms. of K_2SO_4 contain 1·6375 grms. of potassium, 1·844 grms. of $K_2S_2O_3$ contain 0·757 grm. of potassium; therefore, more than one-third, nearly one-half, of the potassium of the $K_2S_{4·67}$ in the original solution appears after treatment with cupric oxide as potassic hyposulphite.

The presence of potassic hyposulphite is assumed on account of the behaviour of the liquid with iodine solution. A direct proof of its presence appeared to be desirable.

Reactions of the filtrate of the cupric oxide.

a. Hydric chloride caused turbidity after some time, probably from sulphur.

b. Barium chloride, a white precipitate, only partly soluble in hydric chloride.

c. Cupric sulphate gave after neutralisation with acetic acid a blue precipitate, which turned dark brown at 70–80° C.

A mixture of sodic hyposulphite, potassic acetate and cupric sulphate behaved in a similar manner.

d. Lead acetate and silver nitrate, respectively, gave the same reactions as they do with a solution of sodic hyposulphite.

122 cub. centims. of the strongly alkaline filtrate were neutralised with acetic acid and allowed to evaporate over hydric sulphate under the receiver of an air-pump. After a few days a great number of prismatic crystals were observed. These crystals warmed with alcohol fused into an oily liquid, which recrystallised on cooling and did not dissolve in alcohol.

Alcohol added to the mother liquor of the crystals produced a crystalline precipitate.

The original crystals, and the crystalline precipitate united weighed 2·634 grms.

According to the determination with iodine solution 122 cub. centims. of the filtrate from the cupric oxide, contain 2·249 grms. anhydrous, or 2·604 grms. hydrated salt of the formula $3K_2S_2O_3, 5H_2O$. The crystals dissolved easily in 3 cub. centims. of water with absorption of heat; from this solution 2·457 grms. of salt were reobtained.

0·497 grm. of the same, dissolved in water and mixed with a solution of strontium chloride, gave, after two days' standing, a very small precipitate.

0·903 grm. of the salt, dissolved in 50 cub. centims. of water, gave, on addition of 1 grm. of barium chloride a white precipitate, which left, after treatment with boiling water, 0·017 grm. of barium sulphate. The filtrates of the barium sulphate yielded a fine crop of barium hyposulphite.

As this salt is, according to my experience, easily obtained in a pure form, the whole of the potassium hyposulphite was converted into the barium compound for the following analytical determinations.

0·882 grm. baric hyposulphite boiled with hydric nitrate gave 0·763 grm. of baric sulphate; the filtrate of this gave, on addition of barium chloride, another quantity of the same salt, which, after ignition and treatment with hydric chloride, weighed 0·753 grm.

Therefore in 100 parts :

	Experiment.	Theory. BaS_2O_3	Theory. BaS_2O_3, H_2O.
Barium	50·86	51·70	48·41
Sulphur	23·60	24·15	22·61

The potassium salt from which the barium hyposulphite had been prepared gave the following reactions :—

a. Hydric chloride produced, a few moments after its addition, a slightly yellow turbidity.

b. Cupric sulphate gave a slight turbidity at common temperatures, on boiling, a copious brown precipitate.

c. Lead acetate, a white precipitate, which did not change its colour at 100° C.

d. Ferric chloride gave the usual violet colour.

e. Silver nitrate, a white precipitate, which turned black at higher temperatures.

According to these experiments there can be no doubt that, by the treatment of a solution of a mixture of potassic penta- and tetra-sulphides with cupric oxide, large quantities of potassic hyposulphite are formed.

The mother liquor of the potassic hyposulphite, from which this salt had been removed by means of alcohol, was left to evaporate in vacuo. The crystalline residue, heated in a platinum crucible, produced an oily liquid, which crystallised on cooling, like potassic acetate, and weighed 2·616 grms.

It was converted by means of hydric sulphate into 2·404 grms. of potassic sulphate.

2·616 grms. of potassic acetate should give, according to theory, 2·320 grms. of potassic sulphate. If we assume that, in the solution obtained by the treatment of potassic polysulphides with cupric oxide, only potassic hyposulphite and potassic hydrate are present, then, according to the numbers given on page 536, 122 cub. centims. of the filtrate from the cupric oxide should have given 2·697 grms. potassic acetate, instead of 2·616 as found by experiment.

Hence, we may conclude that 100 cub. centims. of the filtrate from the cupric oxide contain :

1·844 grms. potassic hyposulphite,
1·263   ,,   ,,   hydrate,

and a very small amount of potassic sulphate.

At my request, Mr. COWPER digested solutions of the other sulphides of potassium with cupric oxide and examined the products for potassium hyposulphite. He found that in a solution of potassic tersulphide (K_2S_3) nearly $\frac{1}{2}$, in one of potassic disulphide about $\frac{1}{5}$, and in one of potassic sulph-hydrate about $\frac{1}{12}$ of the potassium appears after treatment with cupric oxide as hyposulphite. All these experiments lead to the conclusion that the potassic hyposulphite found in solid powder residues by BUNSEN and SCHISCHKOFF's method had been formed during the analysis of the said residues, and was not one of the original products of explosion. This conclusion is supported by the observation of PAPE,* according to which potassic hyposulphite is decomposed at 225° C. into sulphate and pentasulphide of potassium.

At the conclusion of my experiments in July 1879, I communicated the results to Mr ABEL, and he has since then confirmed my observations.

NOBLE and ABEL say at the end of their second memoir (Phil. Trans., 1880, p. 277), " that although it would seem that in certain cases and under certain exceptional circumstances potassium hyposulphite does exist as a secondary, it exists in no case as a primary product, and should not, therefore, be reckoned among the normal constituents of powder residues."

Wishing to obtain a clear conception of the mode of action of cupric oxide in the analysis of a powder residue, I instituted the following experiments :—

6·157 grms. potassic sulphate, and 8·541 grms. of potassic carbonate were dissolved in 100 cub. centims. of water ; the solution filled the space of 103·5 cub. centims.

10 cub. centims. of this liquid were mixed with 5 cub. centims. of a solution containing :

$$\text{Potassium} \quad . \quad . \quad . \quad . \quad . \quad . \quad 0\cdot389 \text{ grm.}$$
$$\text{Sulphur} \quad . \quad . \quad . \quad . \quad . \quad . \quad 0\cdot498 \text{ „}$$

or 3·12 atoms of sulphur for every 2 atoms of potassium.

The solution so prepared was then digested for two days with previously ignited cupric oxide in a well-stoppered bottle, at ordinary temperatures.

The mixture appeared brown, but became decolorised at 35° C.

The contents of the bottle were placed upon a filter ; the black oxide and sulphide were well washed with boiling water, and both, filtrate and wash water united, were kept in a stoppered bottle. They filled the space of 578 cub. centims.

111 cub. centims. of the filtrate required 3·7 cub. centims. of the iodine solution.

192 cub. centims. of the filtrate required 6·3 cub. centims. iodine liquid. Hence, the entire filtrate contained 0·3623 grm. of potassic hyposulphite.

91 cub. centims. of the filtrate acidulated with hydric chloride, boiled for some minutes, separated from precipitated sulphur by filtration, and mixed with baric

* Pogg. Ann., Bd. cxxii., p. 408.

chloride, gave a precipitate of baric sulphate weighing 0·158 grm. The whole filtrate therefore contains 0·749 grm. of potassic sulphate.

91 cub. centims. of the filtrate, acidulated with hydric chloride and evaporated to dryness, gave, after treatment of the residue with hydric sulphate, 0·395 grm. potassic sulphate. From this number it follows that the entire filtrate contained 1·124 grms. of potassium.

91 cub. centims. of the filtrate gave, with manganous sulphate, a precipitate, which generated with dilute hydric sulphate 0·042 grm. of carbonic acid. 578 cub. centims. of the filtrate contain 0·266 grm. carbonic acid, corresponding to 0·834 grm. potassic carbonate.

From the solution of the precipitate caused by manganous sulphate, 0·094 grm. of Mn_3O_4 was obtained, corresponding to 0·597 grm. for the entire filtrate; 0·461 grm. of this is derived from manganous carbonate, the remainder, 0·136 grm. of Mn_3O_4, from the manganous hydrate precipitated by potassic hydrate. 0·136 grm. of Mn_3O_4 corresponds to 0·139 grm. of potassium or 0·310 grm. of K_2S_3. The black cupric oxide and sulphide was dissolved in concentrated hydric nitrate and the solution precipitated by baric chloride; the weight of the baric sulphate was found to be 2·754 grms.

The following table contains the results of these experiments :—

	Composition of the original solution.	Found by analysis.
Potassic carbonate	0·829	0·834
„ sulphate	0·597	0·749
„ tersulphide	0·887	0·310
„ hyposulphite . . .	0·000	0·362
Potassium	1·124	1·124
Sulphur in CuO	0·000	0·378
„ in $K_2S_2O_3$	0·000	0·122

A considerable error attaches to the determination of the sulphur. The cupric oxide had been ignited in a Hessian crucible. From this, it appears, it became contaminated with silica and alumina. The baric sulphate, precipitated from the solution of the cupric oxide in hydric nitrate by baric chloride, contained a copper compound which I regard as a silicate, since it could not be got rid of even after long continued boiling with hydric chloride.

The analysis gives quite a wrong idea of the composition of the original solution. Not only is a portion of the potassic tersulphide converted into hyposulphite, it even appears that some has been oxidised into sulphate.

The following experiments prove the absence of sulphates in the reagents used for the above determinations.

15 cub. centims. of the solution of potassic tersulphide, acidulated with hydric

chloride, boiled, filtered and precipitated with baric chloride gave only 0·0005 grm. baric sulphate. 80 grms. of cupric oxide were dissolved in hydric chloride and the solution mixed with 1 grm. of baric chloride; even after two days' standing no precipitate could be observed.

0·854 grm. potassic carbonate, examined in a similar manner, was found to contain only 0·0007 grm. of sulphate.

1 grm. of sodic hyposulphite in 100 cub. centims. of water gave with barium chloride a crystalline precipitate which proved to be completely soluble in boiling water. Baric chloride, added to the water used in the experiments, and hydric chloride caused no precipitate.

1 grm. of sodium hyposulphite was dissolved in 200 cub. centims. of water, hydric chloride added, and the solution boiled during three-quarters of an hour.

Baric chloride precipitated 0·022 grm. of baric sulphate. Another similar experiment yielded 0·028 grm. baric sulphate.

From these experiments it is clear that in a solution containing hyposulphites and sulphates, the latter cannot accurately be determined by the ordinary method. The error from this source is, however, not sufficiently great to account for the discrepancy between the sulphate taken and found in the experiment described on page 539, and exhibited in the table given on that page.

Accordingly, it appears probable that by the action of cupric oxide upon potassic tersulphide, in *presence of potassic carbonate*, not only potassic hyposulphite but also potassic sulphate is formed.

15 cub. centims. of a solution of potassic sulphide were acidulated by addition of hydric chloride, and by boiling and filtration were separated from the precipitated sulphur. The potassic chloride left, after evaporation of the filtrate from the sulphur, was converted, by means of hydric sulphate, into potassic sulphate. The weight of this salt was found to be 2·554 grms.

5 cub. centims. of potassic sulphide solution, mixed with potassic hydrate and oxydised by chlorine, yielded 3·58 grms. of baric sulphate. 10 cub. centims. of potassic sulphide solution, precipitated by zinc sulphate, and the filtrate from the zinc sulphide examined by means of iodine solution for hyposulphites, gave numbers which indicated in 15 cub. centims. of the sulphide solution 0·114 grm. of potassic hyposulphite. Sulphuric acid was not found in the sulphide solution.

15 cub. centims. of potassic sulphide solution, out of the same bottle from which the quantities used in the above experiments had been taken, were mixed with solutions of 1·188 grms. of potassic sulphate, and of 1·650 grms. of potassic carbonate.

The mixture so prepared had the following composition :—

	Grms.		
Potassic carbonate . . .	1·650		
„ sulphate. . . .	1·188		Grms.
„ sulphide. . . .	2·534 {	Sulphur . .	1·4366
		Potassium .	1·0977
„ hyposulphite . .	0·114 {	Sulphur . .	0·0384
		Potassium .	0·0468

It was digested for a few days in a closed flask with 40 grms. of cupric oxide at common temperatures, and finally decolorised by the raising of its temperature for a short time to 35° C.

The contents of the flask were placed upon a filter and the oxide and sulphide washed with hot water. The volume of filtrate and wash water measured 1081 cub. centims.

The analysis of the liquid gave the following results :—

200 cub. centims. gave 0·394 grm. of baric sulphate ; according to these numbers 1081 cub. centims. contain 1·589 grms. of potassic sulphate.

312 cub. centims. were precipitated with manganous sulphate. From the precipitate so obtained, 0·140 grm. of carbonic acid was developed by means of sulphuric acid, and 0·443 grm. of Mn_3O_4, prepared by the usual method. Hence, 1081 cub. centims. of filtrate contain 1·521 grms. of potassic carbonate and 0·708 grm. of potassium in the form of hydrate.

139 cub. centims. of the liquid required 6·4 cub. centims. of iodine solution. Therefore, 1081 cub. centims. contain 0·945 grm. of potassic hyposulphite.

200 cub. centims., evaporated with concentrated sulphuric acid, gave 1·069 grms. of potassic sulphate, containing 0·4793 grm. of potassium, or in 1081 cub. centims. 2·590 grms. of potassium.

From these data we find the following composition for the solution :—

	Composition of original solution.		Composition according to analysis.	
Potassic carbonate	1·650		1·521	
„ sulphate	1·188		1·589	
„ sulphide	2·534 {	S = 1·4366	1·633 {	S = 0·925
		K = 1·0977		K = 0·708
„ hyposulphite . . .	0·114 {	S = 0·0384	0·945 {	S = 0·318
		K = 0·0468		K = 0·387
Potassium	2·609		2·590	

The mixture of cupric oxide and sulphide, dissolved in concentrated nitric acid, yielded 8·16 grms. of baric sulphate, corresponding to 1·120 grms. of sulphur.

	Sulphur.	
	Contained in original solution.	Found by analysis.
Potassic sulphate	0·2180	0·291
„ sulphide	1·4366	..
„ hyposulphite . . .	0·0384	0·318
Cupric oxide	0·0000	1·120
	1·693	1·729

From these experiments we conclude that by treatment of a solution containing potassic tersulphide, carbonate, and sulphate with cupric oxide, not only potassic hyposulphite but also potassic sulphate is formed.

Experiments with potassic monosulphide.

A solution of 5 grms. of pure potassic hydrate, in 100 cub. centims. of water, was divided into two equal parts, one of these was saturated with sulphuretted hydrogen and then mixed with the other.

20 cub. centims. of this solution gave, after evaporation with hydric chloride, 1·1015 grms. of neutral potassic chloride, corresponding to 0·812 grm. of potassic monosulphide (K_2S).

20 cub. centims. of the solution of the monosulphide were mixed with 2·219 grms. of potassic carbonate and 0·950 grm. of sulphate, and the mixture digested with pure cupric oxide at common temperatures, in a stoppered bottle, until all the potassic sulphide had been decomposed.

The contents of the bottle were treated in the same manner as in former experiments.

The filtrate of the cupric oxide measured 415 cub. centims.

160 cub. centims. required 2·1 cub. centims. of the iodine solution, therefore we have, in 415 cub. centims of the filtrate, 0·103 grm. of potassic hyposulphite.

It was ascertained, by special experiment, that the original potassic monosulphide did not contain hyposulphite.

60 cub. centims. of the liquid gave 0·185 grm. of baric sulphate, corresponding to 0·953 grm. of potassic sulphate in 415 cub. centims. of the filtrate.

100 cub. centims. gave with manganous sulphate a precipitate from which 0·174 grm. of carbonic acid and 0·428 grm. of Mn_3O_4 were obtained. It follows from these numbers that 415 cub. centims. of filtrate contain 0·758 grm. of monosulphide and 2·261 grms. of carbonate of potassium.

40 cub. centims. of the filtrate evaporated with hydric chloride, and the remaining potassic chloride converted by means of hydric sulphate into potassic sulphate, gave

0·482 grm. neutral potassic sulphate. Hence, 415 cub. centims. contain 2·238 grms. of potassium.

From the solution of the cupric oxide and sulphide in concentrated hydric nitrate, 1·684 grms. of baric sulphate were precipitated; 1·684 grms. of baric sulphate contain 0·231 grm. of sulphur.

	Composition of original substance.	Found by analysis.
Potassic carbonate	2·219	2·261
„ sulphate	0·950	0·953
„ monosulphide . .	0·812 $\begin{cases} K=0.5765 \\ S=0.236 \end{cases}$	0·758 $\begin{cases} K=0.538 \\ S=0.220 \end{cases}$
„ hyposulphite . .	0·000	0·103 S = 0·034
Potassium	2·255	2·238
Sulphur in cupric oxide . .	0·000	0·231

From these experiments it follows, as a general result, that if a solution containing potassic sulphate, carbonate and mono- ter- or pentasulphide of potassium is digested with pure cupric oxide, the determination of the potassic carbonate yields in all cases a nearly correct result, also for the sulphate an accurate value is obtained in a solution which contains the sulphide as monosulphide, but the numbers found for potassic sulphides are always incorrect. The potassium hyposulphite is formed by the action of cupric oxide upon pentasulphide of potassium in such quantities that a convenient method for the preparation of the salt might be based on the reaction.

Probably all the potassic hyposulphite, which was found in powder residues by BUNSEN and SCHISCHKOFF's method of analysis, was formed during the analytical operations by the oxidation of potassic sulphide by the oxygen of the cupric oxide. At all events, we cannot assume that potassic hyposulphite is one of the products of the explosion of gunpowder, because at 225° C. it decomposes, according to PAPE, into potassic sulphate and pentasulphide, and because in later experiments, in which zinc chloride was used instead of cupric oxide, NOBLE and ABEL found very little potassic hyposulphite. We are, therefore, justified in replacing the hyposulphite of the analyses of NOBLE and ABEL by its equivalent quantity of potassic sulphide.

The values found by means of BUNSEN and SCHISCHKOFF's method for the potassic sulphate would be correct if the powder residues contained only potassic monosulphide. But as, according to LINCK's and NOBLE and ABEL's experiments, they contain one of the higher sulphides, it is not improbable that a portion of the sulphate observed has been formed during the treatment with cupric oxide from one of the said sulphides, or by the decomposition of potassic hyposulphite during the process of analysis.

The following considerations indicate how this possible error can be corrected :—

If powder is burnt in the apparatus of NOBLE and ABEL, all the oxygen of the decomposed saltpetre is incorporated in the potassic carbonate and sulphate, the

carbonic acid and oxide, and these, together with the potassic sulphide, nitrogen and free sulphur amount to about 96 per cent. of the exploded powder. The following calculation leads to the conclusion that the oxygen of the charcoal and of the moisture in the powder does not enter into the composition of the principal products of explosion, but is eliminated in union with hydrogen in the form of water.

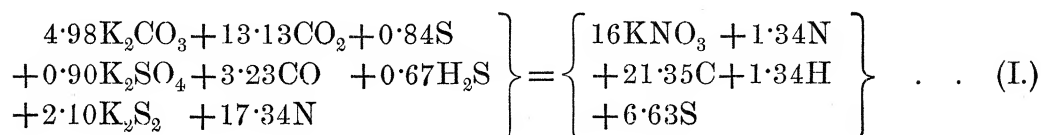According to analysis, the composition of the F. G. powder is represented by the symbols

$$16KNO_3 + 0{\cdot}044K_2SO_4 + 6{\cdot}88S + 20{\cdot}81C + 10{\cdot}78H + 3{\cdot}52O$$
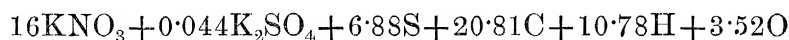
if ash and moisture of the charcoal are left out of consideration. In Experiment 17 of NOBLE and ABEL the hydrogen in ammonic carbonate, sulphuretted hydrogen, and in a free state, added together is equal to 4·1 atoms. This number deducted from 10·78 atoms, the hydrogen of the charcoal, leaves as difference 6·68 atoms. These 6·68 atoms of hydrogen must have formed water, for which operation 3·34 atoms of oxygen, or almost the exact quantity contained in the charcoal, is required.

Also the moisture of the powder cannot have contributed any oxygen, because if it had, an equivalent quantity of hydrogen ought to have been set free, or entered into combination with nitrogen, carbon, or sulphur. And as in all other experiments of NOBLE and ABEL, executed with F. G. powder from Waltham Abbey, the number of atoms of hydrogen, free or combined, which occur amongst the products of combustion, is less than 4·1, it follows, that in these other experiments also the oxygen of the charcoal or of the moisture of the powder has taken no part in the explosion. And finally, since several hundred grammes of powder were exploded in a *hermetically* closed steel cylinder, oxygen from the atmosphere cannot have entered into the composition of products of combustion of the powder.

If, then, we find in one of the experiments, after the potassic hyposulphite has been replaced by its equivalent of potassic sulphide, that the sum of the quantities of oxygen contained in the potassic carbonate and sulphate, carbonic acid, and oxide exceeds the oxygen derived from the decomposed saltpetre, we may assume that this excess of oxygen is owing to some sulphate which had been formed during the process of analysis, and, accordingly, we shall be justified in deducting this excess of sulphate from the total quantity found.

The errors which have been explained on p. 533, due to the mode of calculation, will compensate each other, if the *mean of all the experimental results* be taken.

If all these corrections are carried out we obtain in the form of a chemical equation an approximately correct expression of the metamorphosis of the powders of Waltham Abbey. This equation, deduced from the 31 experiments published by NOBLE and ABEL, is :

$$\left.\begin{array}{l} 4\cdot98K_2CO_3 + 13\cdot13CO_2 + 0\cdot84S \\ +0\cdot90K_2SO_4 + 3\cdot23CO \quad +0\cdot67H_2S \\ +2\cdot10K_2S_2 \quad +17\cdot34N \end{array}\right\} = \left\{\begin{array}{l} 16KNO_3 \quad +1\cdot34N \\ +21\cdot35C + 1\cdot34H \\ +6\cdot63S \end{array}\right\} \quad . \quad . \quad (I.)$$

The powder constituents on the right-hand side of the sign of equality have been calculated from the composition of the products of explosion.

The same constituents, as found by the direct analysis of the powders, are represented by the symbols :
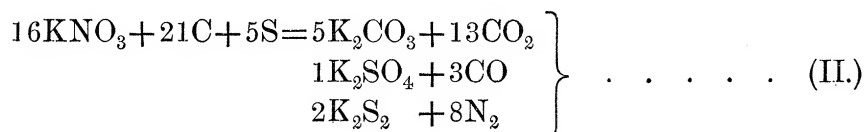
$$16KNO_3 + 21\cdot18C + 6\cdot63S$$
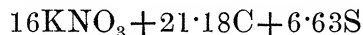
which are in close agreement with those deduced from the products of explosion. Powder of this composition, burnt according to the method of NOBLE and ABEL, will form the products of explosion in quantities as represented by equation (I.), if the small quantities of secondary products arising from the presence of hydrogen in charcoal, such as marsh gas, ammonia, and free hydrogen, are neglected.

The sulphuretted hydrogen is either the product of the direct union of hydrogen and sulphur at comparatively low temperatures, or of the action of carbonic acid and water upon potassic sulphide. In either case its formation has no direct connexion with the explosion, and it ought to be likewise omitted from an equation representing the metamorphosis of gunpowder.

0·84 atom of sulphur is represented as free, because there are no data to show how much sulphur has united with the iron of the apparatus.

It is usual to represent the potassic sulphide as monosulphide. Further on it will be shown that this is not correct, but that disulphide is really produced.

We may then replace equation (I.) by the more simple one

$$\left.\begin{array}{l} 16KNO_3 + 21C + 5S = 5K_2CO_3 + 13CO_2 \\ 1K_2SO_4 + 3CO \\ 2K_2S_2 \quad +8N_2 \end{array}\right\} \quad . \quad . \quad . \quad . \quad . \quad (II.)$$

A portion of the sulphur of the powder has united with hydrogen and iron, hence the difference of sulphur in equations (I.) and (II.).

A powder consisting of

$$16KNO_3 + 21C + 5S$$
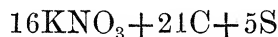
exploded according to the method of NOBLE and ABEL in a vessel the substance of which is not attacked by the products of combustion, ought, *cæteris paribus*, to yield the products of explosion always in the proportions represented in equation (II.).

Under very great pressures the amount of carbonic oxide appears to diminish to a small extent ; this variation of the carbonic oxide has, however, only a slight influence

on the other products, amounting in the case of potassic carbonate, potassic sulphate, and potassic disulphide generally to less than 0·1 of a molecule.   (See note, p. 526.)

Equation (II.) expresses only the quantitative relations between the powder constituents and the products of explosion; the reactions which occur during explosion, which of them are simultaneous, and the order in which they succeed each other have still to be determined.

The solid products of explosion possess the composition and the properties of liver of sulphur prepared with an insufficient quantity of sulphur.   We can conceive that, at first, all the potassium of the saltpetre forms with carbon and oxygen potassic carbonate, and that, in another stage, sulphur acts on the potassic carbonate and produces the mixture known as the solid powder residue.   Or we may conceive that potassic sulphate is the first product, and that this is afterwards reduced by carbon to potassic disulphide and carbonate.   Both conceptions would lead to the same results.

The experiments of KAROLYI,* executed more than 17 years ago, contain the key to a chemical theory of gunpowder, and allow us to form an idea of the nature of the reactions, and the order in which they follow each other during the combustion of powder.   He proposed to himself to decide by experiment whether or not the nature of the products and their relative quantities are dependent on the pressure which obtains during explosion.   CRAIG† had asserted that under great pressure, such as would exist during the explosion in a piece of ordnance, much more potassic sulphide was formed than had been obtained by BUNSEN and SCHISCHKOFF under ordinary atmospheric pressure.   KAROLYI took 36·836 grms. of Austrian cannon powder, which had, according to his opinion, a composition similar to that of the powder employed by BUNSEN and SCHISCHKOFF, and enclosed the same in a small metallic cylinder, suspended in the centre of a 60-pounder hermetically closed shell.   The air was then pumped out of the shell by means of an air pump, and the powder exploded by an electric current.   As soon as the pressure of the gases in the cylinder had attained a certain magnitude the cylinder burst, and its contents were scattered about the space of the exhausted shell.

The capacity of the shell and the amount of powder had been so adjusted that after explosion the gases in the shell should possess a tension of about 1·5 atmospheres; they were allowed to escape into tubes and sealed up for analysis.   The solid products, which were removed from the shell by means of water, as well as the gases, were examined by the methods of BUNSEN.

A similar experiment was made with 34·153 grms. of rifle powder.

* Pogg. Ann., Bd. cxviii., p. 544.

† SILIMAN's Am. J., [2], vol. xxxi., p. 429; Chem. News, vol. iv., p. 18.

COMPOSITION of the powders.

	Cannon powder.	Rifle powder.
Saltpetre.	73·78	77·15
Sulphur	12·80	8·63
Charcoal—		
Carbon	10·88	11·78
Hydrogen	0·38	0·42
Oxygen	1·82	1·79
Ash	0·31	0·28

COMPOSITION of the products of explosion.

	Cannon powder. Grms.	Rifle powder. Grms.
Potassic carbonate	7·14	7·096
,, sulphate	13·61	12·354
,, hyposulphite	1·04	0·605
,, sulphide	0·04	0·000
Carbonic acid	6·40	7·442
,, oxide	0·97	0·504
Nitrogen	3·60	3·432
Hydrogen	0·04	0·047
Marsh gas	0·15	0·167
Sulphuretted hydrogen	0·10	0·079
Carbon	0·94	0·887
Sulphur	1·73	0·397
Ammonic carbonate	0·99	0·908
Loss	0·08	0·235

Cannon powder gave 30·77 per cent. of gas and 69·25 per cent. solid residue. Rifle powder gave 34·86 per cent. of gas, and 65·14 per cent. solid residue.

KAROLYI, comparing his results with those of BUNSEN and SCHISCHKOFF, arrives at the conclusion that the nature and quantities of the products of explosion are not much influenced by the conditions under which the combustion takes place, but that the composition of the powder determines in a great measure the proportions in which the products of explosion are formed. Besides this, he deduces no other conclusions from his experiments. KAROLYI's observations do not support CRAIG's assertion; the pressure in the metallic cylinder before explosion must have been great, yet very little or no potassic sulphide has been formed.

A few years later (1869) FEDOROW* published the results of some experiments executed by him on the explosion of gunpowder. He, like CRAIG, concludes that

* Zeitschrift für Annalytische Chemie, Bd. ix., p. 127; STRECKER, Jahresbericht, 1869, p. 1059.

under high pressure more potassic sulphide is produced than would be formed by the same powder under lower pressures.

The experiments of FEDOROW, however, do not prove anything of the kind. He fired powder from a pistol and from a 9-pounder cannon, and it appears that the solid products of the powder fired from the pistol were collected in a glass tube. A charge of 0·75 grm. of powder gave a residue with proportionally more potassic sulphate and less of potassic sulphide than one of 1·5 grms., and relatively still smaller was the potassic sulphate and greater the sulphide in the residue obtained by the firing of 3 lbs. of powder from the cannon.

M. FEDOROW concludes : " A smaller amount of powder remains unconsumed, less potassic sulphate, but more sulphide and carbonate are formed under higher than under lower pressures. Time acts like pressure. If the combustion of the powder is retarded the same effects follow as if the pressure had been increased. A charge of 1·5 grms. of a mixture consisting of 100 parts of meal powder, and 0·5 part of stearic acid, gave a residue with less potassic sulphate, but with more carbonate and hyposulphite than a similar charge of ordinary powder would have done."

Potassic sulphide is, as is well known, a substance endowed with great attraction for oxygen, not only at high, but also at ordinary temperatures. It appears that the air was not excluded from the glass tube into which M. FEDOROW fired his charges for the collection of the solid residues. A greater percentage of the potassium sulphide formed by a small charge, than of the sulphide of the products of a larger charge, will in this manner be oxidised.

It thus appears that M. FEDOROW's experiments can be explained without reference to pressure. But as far as the retardation of the combustion by stearic acid is concerned, we cannot ascribe to retardation an effect which is due to the stearic acid itself. Stearic acid at a red heat reduces potassic sulphate to sulphide and probably carbonate.

M. FEDOROW could not collect and examine the gases.

The experiments of FEDOROW do not establish a relation between pressure and the nature and quantities of the products of explosion, and, consequently, do not invalidate the conclusions of KAROLYI, as stated on page 547.

We will now proceed to explain, by means of the analytical results of KAROLYI, some of the reactions which take place during the combustion of gunpowder. For this purpose it will be desirable to express the composition of the Austrian powders, and the products of explosion, by chemical formulæ.
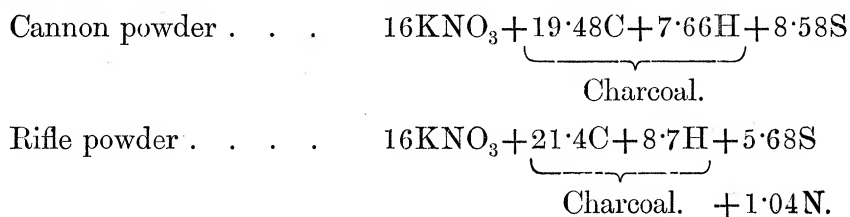
COMPOSITION of the powders.

	Cannon powder.	Rifle powder.
Saltpetre	16·00 mols.	16·00 mols.
Sulphur.	8·70 atoms.	5·66 atoms.
Carbon	19·80 ,,	20·57 ,,
Hydrogen	8·32 ,,	8·80 ,,
Oxygen.	2·50 ,,	2·34 ,,

COMPOSITION of the products of combustion of quantities of powder which contain 16 mols. of saltpetre.

	Cannon powder.	Rifle powder.
Potassic carbonate . . .	3·05 mols.	3·27 mols.
,, sulphate . . .	4·61 ,,	4·52 ,,
,, hyposulphite . .	0·31 ,,	0·20 ,,
,, sulphide . . .	0·01 ,,	0·00 ,,
Carbonic acid*	9·23 ,,	11·46 ,,
,, oxide	2·04 ,,	1·15 ,,
Nitrogen	7·55 ,,	8·06 ,,
Sulphuretted hydrogen .	0·17 ,,	0·14 ,,
Hydrogen.	2·36 atoms.	3·01 atoms.
Marsh gas	0·55 mol.	0·67 mol.
Ammonia.	0·92 ,,	0·91 ,,
Carbon	4·61 atoms.	4·74 atoms.
Sulphur	3·16 ,,	0·79 ,,

Calculated from the products of combustion, we obtain for

Cannon powder . . . $16KNO_3 + \underbrace{19·48C + 7·66H}_{\text{Charcoal.}} + 8·58S$

Rifle powder . . . $16KNO_3 + \underbrace{21·4C + 8·7H}_{\text{Charcoal.}} + 5·68S \quad +1·04N.$

The potassic carbonate, potassic sulphate, potassic hyposulphite, and potassic sulphide, the nitrogen, carbonic acid, and carbonic oxide added together, amount in the case of the cannon powder to 89·6, and in that of the rifle powder to 92·0 per cent. of the exploded powder. 7·2 per cent. of carbon and sulphur of the cannon powder and 3·7 per cent. of the same elements of the rifle powder, remained free at the end of the explosion. The sum of all the other products, therefore, does not amount to more than 3 or 4 per cent., and as, with the exception of the nitrogen in the ammonia,

* Inclusive of the carbonic acid combined with ammonia.

no constituents of the saltpetre occur in them, they may be regarded as merely accessory products not directly concerned in the explosion.

As the composition of the Austrian service powders does not differ much from that of the powders of Waltham Abbey, it will be interesting to contrast the results of KAROLYI with those obtained by NOBLE and ABEL.

Remarkable differences will be observed if equation (I.), page 545 is compared with the composition of the products of combustion observed by KAROLYI and represented by means of chemical symbols on page 549. Equation (I.), as well as KAROLYI's results, are calculated for quantities of powder containing 16 mols. KNO_3.

NOBLE and ABEL, according to equation (I.), found about a quarter of the potassium of the decomposed saltpetre as potassic sulphide, whereas in KAROLYI's experiments the sum of the potassium in the hyposulphite, and in the sulphide of the products of combustion of cannon powder amounted to only $\frac{1}{26}$th, and in that of the rifle powder only to $\frac{1}{40}$th of the potassium of the saltpetre of the exploded powder. It seems to follow that the production of such small quantities of potassic hyposulphite and sulphide cannot be the direct result of the chief reactions of the explosion. KAROLYI obtained much more potassic sulphate and less potassic carbonate than the English chemists; a considerable quantity of the carbon of his powders remained unconsumed, whilst in NOBLE and ABEL's experiments, as a rule, every trace of this element was burnt, although the English powders contain somewhat more carbon than the Austrian. Similar differences occur between the results obtained with the gaseous products. The gases obtained by KAROLYI were combustible, those of NOBLE and ABEL were not. The gases from the Austrian powders contained more hydrogen and marsh gas and less sulphuretted hydrogen than those from the mixtures of Waltham Abbey.

	Mean percentage by volume.	
	Austrian.	Waltham Abbey.
Hydrogen	6·41	2·50
Marsh gas	2·86	0·31
Sulphuretted hydrogen . . .	0·76	2·56

KAROLYI inclosed his powders in a thin brass cylinder hermetically closed, and ignited the charge by means of a galvanic current. As soon as the tension of the gases developed by the combustion had reached a certain magnitude the metal cylinder exploded, and its contents were scattered against the cold sides of the exhausted 60-pounder shell. Thus the combustion of the powder was interrupted before its completion. The correctness of this view is rendered apparent if the effect is considered which would have followed if the products of KAROLYI had remained in contact for some time at a red heat. The free carbon and hydrogen, and the constituents of the marsh gas would have been burnt at the expense of the oxygen of the potassic sulphate; the quantity of the latter would have been diminished and

that of the sulphide increased, the free sulphur would have decomposed potassic carbonate with production of potassic sulphate and sulphide ; in short, the products of combustion would have formed in similar proportions as we find them in NOBLE and ABEL's experiments.   The products of several hundred grammes of powder remained in a fluid condition at a white heat in NOBLE and ABEL's steel cylinder from 60 to 100 seconds in contact, whereas the 36 grms. of burning powder were scattered after the explosion of KAROLYI's brass cylinders over the cold sides of a large iron shell, and their combustion occupied only a very small fraction of a second.   The reactions between the powder constituents had time to complete themselves in NOBLE and ABEL's steel cylinder, but they had not in KAROLYI's small brass vessel.   And although the time of the combustion in the experiments of the last-named chemist was very short, less than one second, we find all the saltpetre of the powder decomposed, and its constituents incorporated in the potassium salts, carbonic oxide and carbonic acid, or set free as nitrogen.

At the same time two of the potassium salts, the hyposulphite and sulphide, occur in such small quantities that we may regard them as secondary products, not connected with the chief reactions of the explosion, and accordingly neglect them.

Hence we have, as chief products formed in KAROLYI's experiments : potassic sulphate and potassic carbonate, carbonic acid and nitrogen, and perhaps carbonic oxide.

The combustion of gunpowder accordingly consists of two distinct stages; a process of oxidation, which is finished in a very short time, occupying only a very small fraction of a second, and causing the explosion, and during which potassium carbonate and sulphate, carbonic acid, some carbonic oxide and nitrogen are produced, and a process of reduction, which succeeds the process of oxidation and requires a comparatively long time for its completion.   As the oxygen of the saltpetre is not sufficient to oxidise all the carbon to carbonic, and all the sulphur to sulphuric acid, a portion of the carbon and a portion of the sulphur are left free at the end of the process of oxidation.   The carbon so left free reduces, during the second stage of the combustion, potassic sulphate, and the free sulphur decomposes potassic carbonate. Hydrogen and marsh gas, which are formed by the action of heat upon charcoal, likewise reduce potassic sulphate, and some hydrogen combines with sulphur, forming sulphuretted hydrogen.

Great variations of pressure appear to affect the proportions of the different products in a very slight degree, so that it may be regarded as doubtful whether pressure has any influence on them.

KAROLYI's experiments happen to be arranged in such a manner that the combustion of his powders could only proceed to the end of the first and the commencement of the second stage ; in NOBLE and ABEL's explosions, the reactions of the second stage were also completed.

This view of the combustion of gunpowder explains not only the experiments of

NOBLE, ABEL, and KAROLYI, but is also in perfect accordance with the thermo-chemical relations of the products of explosion.

The heat of formation of a molecule of potassic sulphate is much greater than that of one of potassic sulphide, hence, the production of the former is to be expected during explosion. In short, the formation of the molecules of potassic carbonate, potassic sulphate, and carbonic acid is accompanied by the greatest evolution of heat.

KAROLYI examined the products of explosion according to BUNSEN and SCHISCH-KOFF's method, which does not yield exact values for potassic sulphide and sulphate. The errors arising from this source will, however, be very small, if the potassic sulphide in the original powder residue is small. The small amount of potassic hypo-sulphite found by KAROLYI proves that the products of combustion contained, in his experiments, very little potassic sulphide. As the potassic hyposulphite must be regarded as a product of oxidation of the potassic sulphide, it has been replaced in the following calculations by its equivalent of potassic sulphide. Nevertheless, the quantity of the latter does not exceed 0·32 of a molecule, hence the error caused by the method of analysis may be neglected.

We will now take the chief products of explosion observed by KAROLYI, and calculate from their composition the quantities of powder constituents which took part in their formation, and arrange the results in form of equations.

| CANNON powder.			RIFLE powder.	
$3{\cdot}05\ K_2CO_3$	$16\quad KNO_3$		$3{\cdot}30\ K_2CO_3$	$16\quad KNO_3$
$4{\cdot}62\ K_2SO_4$	$14{\cdot}32\ C$		$4{\cdot}49\ K_2SO_4$	$15{\cdot}94\ C$
$0{\cdot}33\ K_2S_2$	$5{\cdot}28\ S$		$0{\cdot}20\ K_2S_2$	$4{\cdot}89\ S$
$9{\cdot}23\ CO_2$	$-0{\cdot}9\ N$		$11{\cdot}49\ CO_2$	$3{\cdot}99\ O$
$2{\cdot}04\ CO$	$0{\cdot}13\ O$		$1{\cdot}15\ CO$	
$7{\cdot}55\ N_2$			$8{\cdot}00\ N_2$	

The entire quantity of saltpetre contained in the powders taken for these experiments was decomposed, and its constituents, with the exception of very small quantities of potassium and nitrogen, in potassic sulphocyanate and ammonia, reappear in the above chief products. The cannon powder contains for every 16 mols. of KNO_3 about 3 atoms of sulphur more than the rifle powder (p. 549). Nevertheless, during the first stage of the combustion the quantities of sulphur consumed in the formation of potassic sulphate are nearly the same in the experiments with both powders, and the potassic carbonate and disulphide are also almost identical.

The ratios of the oxygen in the potassic carbonate, sulphate, and carbonic acid are as follows :—

| | Oxygen. | | |
	K_2CO_3	K_2SO_4	CO_2
Cannon powder	9·15	18·44	18·46
	1	2	2
Rifle powder	9·90	17·96	22·98
	1	1·81	2·33

The amount of oxygen in the products of explosion of the rifle powder has been found about 1·2 per cent. too high, consequently an error attaches to one or more of the analytical determinations.

The metamorphosis of the cannon powder during the first stage of the combustion can almost exactly, that of the rifle powder approximately, be represented by the equation

$$10(KNO_3) + 8C + 3S = 2(K_2CO_3) + 3(K_2SO_4) + 6(CO_2) + 5(N_2) \quad . \quad . \quad (III.)$$
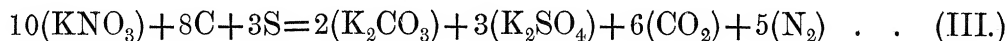
It is worthy of notice that the ratios of the oxygen in the three principal products, potassic carbonate, potassic sulphate, and carbonic acid, are, according to equation (III.), of all possible ratios the most simple, if these products are to be formed by the combustion of a mixture of saltpetre, carbon, and sulphur.

From these considerations it appears to follow that during the explosion of gunpowder, or the first stage of its combustion, the constituents of powders which differ in their composition will act on each other in certain fixed stöchiometrical proportions.

It may be assumed as highly probable that of the infinite number of mixtures, which can be prepared from saltpetre, carbon, and sulphur, some will be more combustible than others, and, among the more combustible mixtures, one will be found containing the constituents in proportions most favourable for their transformation into the chief products of explosion. In this most combustible mixture the number of the molecules of saltpetre and of the atoms of carbon and sulphur will probably stand in simple arithmetical relations to each other, and if a mixture containing the constituents in other proportions be ignited, they will tend to react on each other in the stöchiometrical proportions of the most combustible mixture.

Equation (III.) can be transformed into :

$$16KNO_3 + 12·8C + 4·8S = 3·2K_2CO_3 + 4·8K_2SO_4 + 9·6CO_2 + 8N_2$$

and as during the first stage of the combustion some carbonic oxide is probably also formed, we may write the equation instead

$$16KNO_3 + 13C + 5S = 3K_2CO_3 + 5K_2SO_4 + 9CO_2 + CO + 8N_2 \quad . \quad . \quad (IV.)$$

This equation explains the experiments of KAROLYI in a very satisfactory manner.

If the reactions went a little beyond the first stage of the combustion, and we add to the left of the sign of equality 1·32 atoms of carbon, which would reduce some potassic sulphate with formation of potassic sulphide and carbonate, carbonic acid and oxide, according to equations which will be given afterwards, numbers are obtained which are almost identical with those calculated from KAROLYI's observations on the products of explosion of cannon powder (p. 552). The same remark applies to the products of the rifle powder, except the carbonic acid.

The excess of oxygen found in the products of rifle powder indicates that some error has occurred in the determinations of these products, and it seems to have influenced, almost exclusively, the carbonic acid. If the quantity of this substance is calculated according to the available oxygen of the decomposed saltpetre, a number is obtained which agrees very well with equation (IV.).

From the foregoing observations it follows that powders of the composition of the Austrian service powders—

$$16KNO_3 + 19·8C + 8·7S$$
$$\text{and}\quad 16KNO_3 + 20·57C + 5·66S$$
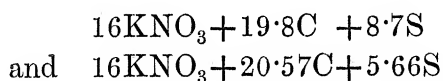
burn during the first stage of the metamorphosis according to the equation:

$$16KNO_3 + 13C + 5S = 3K_2CO_3 + 5K_2SO_4 + 9CO_2 + CO + 8N_2$$
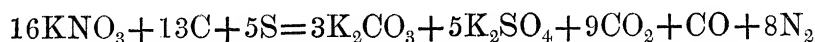
and that the carbon and sulphur which the powders contain, beyond the quantities required by this equation, remain free.

The very combustible sporting powder of BUNSEN and SCHISCHKOFF contained

$$16KNO_3 + 13·3C + 6·3S$$
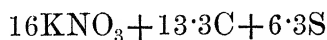
Therefore, it will be seen that the constituents of the service powders react upon each other during the first stage of the explosion nearly in the same stöchiometrical quantities in which they are contained in the more highly combustible sporting powder.

If it be correct that equation (IV.) represents proportions of saltpetre, carbon, and sulphur, in which these substances will burn with greater facility than they do in the proportions of the service powders, then we can by means of equation (IV.) calculate the composition of a powder which shall be distinguished by its great combustibility.

Besides saltpetre, carbon and sulphur, hydrogen, oxygen, ash, and moisture are contained in gunpowder. The weight of these latter constituents is about 4 per cent. of the mixture. If we add 4 per cent. to the quantities represented by the symbols

$$16KNO_3 + 13C + 5S$$
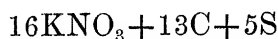
and consider hydrogen, oxygen, ash, and moisture united with carbon to charcoal, we obtain for the percentage composition of the most combustible mixture

$$\text{Saltpetre} \ldots \ldots \quad 80\cdot31$$
$$\text{Sulphur} \ldots \ldots \quad 7\cdot95$$
$$\text{Charcoal} \ldots \ldots \quad 11\cdot74$$

Sporting powders are required to burn quickly, and the composition of some of them approaches very closely to these theoretical values.

	Saltpetre.	Sulphur.	Charcoal.
English*	79·7	7·8	12·5
French	78·0	10·0	12·0
BUNSEN and SCHISCHKOFF's powder .	78·99	9·84	11·17
Sporting powder in the year 1546 .	83·4	8·3	8·3

The heat relations of the products of explosion, as represented by equation

$$16KNO_3 + 13C + 5S = 3K_2CO_3 + 5K_2SO_4 + 9CO_2 + CO + 8N_2,$$
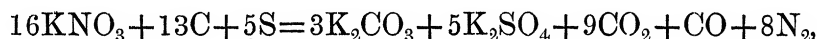
are of special interest.

If we assume for the heat of formation of potassic carbonate, potassic sulphate, and carbonic acid the following values—

$$K_2CO_3 = 279540 \text{ cal.}$$
$$K_2SO_4 = 344640 \text{ ,,}$$
$$CO_2 = 97000 \text{ ,,}$$
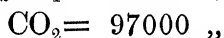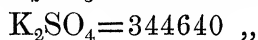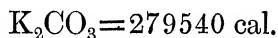
we obtain

$$3 \times 279540 = \ 838620$$
$$5 \times 344640 = 1723200$$
$$9 \times \ 97000 = \ 873000$$
$$838620 : 1723200 : 873000 = 1 : 2\cdot05 : 1\cdot04$$
$$\text{or nearly } 1 : 2 : 1$$

ratios which are very remarkable.

The total amount of heat produced by the combustion of $16KNO_3 + 13C + 5S$ according to equation (IV.), is $= 1563189$ cal. The maximum amount of heat is produced by a mixture which contains for every 16 mols. of saltpetre 8 atoms of carbon and 8 atoms of sulphur, according to the equation :

$$16KNO_3 + 8C + 8S = 8K_2SO_4 + 8CO_2 + 8N_2$$
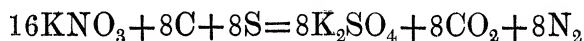
and amounts to 1621450 cal.

Therefore, if the combustion of ordinary service powder takes place during the first stage according to equation (IV.), nearly the maximum quantity of heat is obtained which a mixture of saltpetre, sulphur, and carbon can produce.   If the question were

* GRAHAM-OTTO, 'Lehrbuch der Chemie,' iv. edit., ii., p. 211.

asked: in what proportions must the constituents of a given mixture of saltpetre, carbon, and sulphur react during the process of explosion, and what must be the ratios of the chief products of explosion, so that on one hand the total quantity of heat developed is as great as possible, and, on the other hand, the amounts of heat produced by the formation of the chief products shall stand to each other in a simple relation? the answer would be: the combustion must take place according to equation (IV.).

But not only does this equation correspond to the most simple relations of the heat of formation of the principal products, it likewise requires the most simple distribution of the oxygen of the decomposed saltpetre. If the combustion of a mixture of saltpetre, carbon, and sulphur is to produce potassic carbonate and sulphate, carbonic acid and nitrogen, and if the oxygen of each of the first three products is to stand to the oxygen of the others in the most simple ratios possible, then the mixture must burn according to equation (III.), p. 553, and as the proportions expressed by equation (IV.) closely approach to those of equation (III.), it follows that equation (IV.) fulfils all the conditions and consequences explained in the foregoing lines. And, perhaps, these relations are the cause why mixtures of saltpetre, carbon, and sulphur of different composition burn during the first stage of the explosion according to equation (IV.), and if they contain more carbon and sulphur than is required by this equation, the excess of the two elements will remain free.

These interesting conclusions I deduce from the analytical data of KAROLYI and the corrected results of NOBLE and ABEL's experiments. Their investigations, however, do not give any information about the reactions of the second stage of the combustion of gunpowder, the reduction of potassic sulphate by carbon, and the decomposition of potassic carbonate by sulphur. Hitherto it has been assumed that potassic monosulphide is formed; this is, however, a mistake.

According to BERZELIUS and MITSCHERLICH[*] the products of the decomposition of potassic carbonate by sulphur at a white heat are potassic sulphate and disulphide:

$$4K_2CO_3 + 7S = K_2SO_4 + 3K_2S_2 + 4CO_2$$
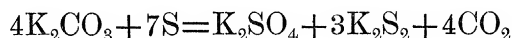
The question we have now to solve is: which of the sulphides of potassium is formed by the action of carbon upon potassic sulphate at a white heat?

BAUER[†] and WITTSTOCK[‡] obtained potassic carbonate and a polysulphide, but the amount of sulphur in the polysulphide was not determined.

A mixture of

26·5 grms. of potassic sulphate
10·54　　,,　　　　　,,　　carbonate
2·5　　,,　　　charcoal

---

[*] GMELIN-KRAUT, 'Handbuch der Chemie,' Bd. ii., p. 39.
[†] Ibid., p. 33.　　　　　　　　　　[‡] Ibid., p. 33.

was exposed in a porcelain crucible for half an hour to a temperature approaching white heat. The contents of the crucible dissolved completely in water, forming a deep yellow solution.

20 cub. centims. of this solution acidulated with hydric chloride, gave a copious precipitate of sulphur, and the filtrate of this precipitate left, after evaporation and treatment with hydric sulphate, 2·943 grms. of potassic sulphate. The potassium of

$$1·960 \text{ grms. potassic sulphate}$$
$$0·779 \quad ,, \qquad ,, \qquad \text{carbonate}$$

of the salts originally taken, is, accordingly, present in 20 cub. centims. of the solution.

20 cub. centims. of the same solution gave by the usual method 1·038 grms. of baric sulphate, corresponding to 0·775 grm. of potassic sulphate.

19·28 cub. centims. of the same solution placed for some days in contact with 5 grms. of cupric oxide and the carbonic acid in the liquid determined according to BUNSEN's method gave 0·37 grm. of this substance, which corresponds to 1·203 grms. of potassic carbonate in 20 cub. centims. of the solution.

1·96 grms. of potassic sulphate originally taken contain 0·36 grm. of sulphur.
0·775 ,,   ,,   ,,   found in 20 cub. centims. contains 0·142 grm. of sulphur.
              Sulphur in potassic sulphide$=0·218$ grm.

20 cub. centims. of the solution contain 1·318 grms. of potassium.

1·203 grms. of potassic carbonate contain 0·680 grm. of potassium, and 0·775 grm. of potassic sulphate 0·347 grm. of potassium; the difference of 0·291 grm. represents the potassium in potassic sulphide.

Hence the potassic sulphide produced by the action of the carbon of the charcoal upon the mixture of potassic sulphate and carbonate contains :

	Grm.
Potassium.	0·291
Sulphur	0·218
	0·509

and the composition of the salts in 20 cub. centims. of the solution of the fused mass is :

	Found.	Taken.
Potassic sulphate	0·775	1·960
,, carbonate	1·203	0·779
,, sulphide	0·509	0·000

The composition of the potassic sulphide can be represented by the symbols

$$K_2S_{1·82}$$

Therefore, potassic sulphate and the carbon of charcoal, react, under the conditions of the experiment, principally according to the equation

$$4K_2SO_4 + 7C = 2K_2CO_3 + 2K_2S_2 + 5CO_2$$
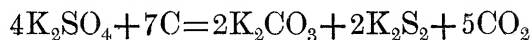
NOBLE and ABEL calculate their potassic sulphide as monosulphide, and in a special column give, as free sulphur, the sulphur not contained in the monosulphide, potassic sulphate and potassic hyposulphite. This so-called free sulphur was in reality contained in the residues partly in union with potassium as disulphide, partly with iron as ferrous sulphide.

If we imagine their free sulphur all combined with their potassic monosulphide, we obtain :

In 15 experiments united to 2 atoms of potassium, from 1·7 to 2·44 atoms of sulphur.

In seven experiments from 2·44 to 3·00 atoms of sulphur.

And in three experiments from 3·0 to 3·7 atoms of sulphur. The mean of 25 experiments would give us for 2 atoms of potassium 2·42 atoms of sulphur. But as a portion of the so-called free sulphur was in union with iron, it follows that in the powder residues 2 atoms of potassium were on an average combined with less than 2·42 atoms of sulphur. These numbers, however, apply only to their corrected results.

According to BERZELIUS and MITSCHERLICH the action of sulphur upon potassic carbonate at a white heat produces K_2S_2 ; the reduction of potassic sulphate in presence of carbonate, according to my own experiments, gives $K_2S_{1·82}$; the mean of NOBLE and ABEL's experiments for the composition of the potassic sulphide formed by the explosion of powder in their apparatus is less than 2·42 atoms of sulphur for every 2 atoms of potassium, hence we may conclude that the potassium sulphide formed during the second stage of the combustion of gunpowder is the disulphide, or at least contains the two elements in a proportion closely approaching the proportion in the disulphide. The following considerations confirm this conclusion.

The mean composition of the English service powder is :

$$16KNO_3 + 21·18C + 6·63S$$
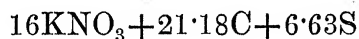
The Austrian rifle powder contains :

$$16KNO_3 + 20·57C + 5·66S$$
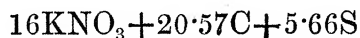
The products of combustion of the former are, according to NOBLE and ABEL,

$$4·98K_2CO_3 + 0·90K_2SO_4 + 2·10K_2S + 13·13CO_2 + 3·23CO + 0·84S$$

Those of the Austrian rifle powder, according to KAROLYI, are

$$3·27K_2CO_3 + 4·52K_2SO_4 + 0·2K_2S_2 + 11·46CO_2 + 1·15CO + 4·74C + 0·79S$$
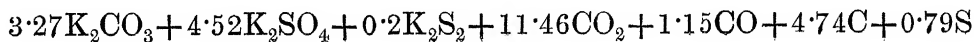
KAROLYI's products contain a considerable amount of free carbon, which element is completely burnt in NOBLE and ABEL's experiments.
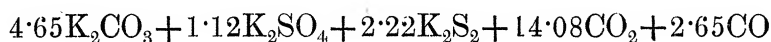
If we now assume that KAROLYI's products had remained in contact at a high temperature, not a fraction of a second, but from one to two minutes, as was the case in NOBLE and ABEL's experiments, the free carbon would have been oxidised by oxygen contained in potassic sulphate, and the free sulphur would have reacted upon the potassium carbonate, and the final result of these reactions would have been a quantitative relationship between the products similar to that found by NOBLE and ABEL. The potassic carbonate, the potassic disulphide, the carbonic oxide, and carbonic acid would have increased, and the quantity of the potassic sulphate would have diminished. But the amount of potassic carbonate could not become greater if the reduction of the sulphate took place according to the equation :

$$K_2SO_4 + 2C = K_2S + 2CO_2$$
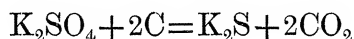
hence, we must assume the formation of potassic disulphide. If we calculate from the analytical data of KAROLYI the proportions of his products on the supposition that the carbon which had remained free had acted on potassic sulphate according to the equation :

$$4K_2SO_4 + 7C = 2K_2CO_3 + 2K_2S_2 + 5CO_2$$

we obtain :

$$4 \cdot 65K_2CO_3 + 1 \cdot 12K_2SO_4 + 2 \cdot 22K_2S_2 + 14 \cdot 08CO_2 + 2 \cdot 65CO$$

quantities which are as near those found for the English powders as the composition of the Austrian rifle powder approaches those of Waltham Abbey.

If the potassic hyposulphite found by BUNSEN and SCHISCHKOFF originated during the analysis of their powder residue, then the latter contained, for 16 mols. of decomposed saltpetre, 0·45 mol. of K_2S_2 and 0·33 mol. of K_2S.

LINCK[*] found, amongst the products of the Würtemberg service powder, only potassic disulphide.

From NOBLE and ABEL's[†] analysis of the products of English mining powder it would follow that for every 16 mols. of decomposed saltpetre, 4 mols. of K_2S are formed and 5 atoms of sulphur left free; this would give us for the composition of the potassic sulphide 2 atoms of potassium and 2·25 atoms of sulphur.

From these facts we conclude that the second stage of the combustion of gunpowder takes place according to the equations :

$$4K_2CO_3 + 7S = K_2SO_4 + 3K_2S_2 + 4CO_2 \quad \cdots \cdots \quad \text{(V.)}$$

$$4K_2SO_4 + 7C = 2K_2CO_3 + 2K_2S_2 + 5CO_2 \quad \cdots \cdots \quad \text{(VI.)}$$

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[*] Ann. der Chemie und Pharm., Bd. cix (1859), p. 53.
[†] Phil. Trans. (1880), p. 207.

The possibility of dissociation requires the additional equation

$$K_2CO_3 + K_2S_2 + O_7 = 2K_2SO_4 + CO_2 \quad \cdot \quad \cdot \quad \cdot \quad \cdot \quad \cdot \quad \text{(VII.)}$$

The final results of the reactions represented by equations (III.), (IV.), (V.), (VI.), and (VII.) can be expressed by one equation.

For this purpose let x, y, and z be positive numbers, and a denote how many molecules of carbonic oxide are formed by the combustion of a quantity of powder containing x molecules of saltpetre, y atoms of carbon, and z atoms of sulphur. The general equation representing the qualitative and quantitative relations between the constituents of a mixture of saltpetre, carbon, and sulphur on the one hand, and the products of *complete* combustion on the other, will then be :

$$
\begin{aligned}
x\,KNO_3 + y\,C + z\,S = \quad & \tfrac{1}{28}[4x + 8y - 16z - 4a](K_2CO_3) \\
& + \tfrac{1}{28}[20x - 16y + 4z + 8a](K_2SO_4) \\
& + \tfrac{1}{28}[-10x + 8y + 12z - 4a](K_2S_2) \\
& + \tfrac{1}{28}[-4x + 20y + 16z - 24a](CO_2) \\
& + \tfrac{1}{2}x\,N_2 \\
& + a\,CO
\end{aligned}
\right\} \quad \cdot \quad \cdot \quad \text{(VIII.)}
$$

As far as the application of this equation is concerned, the following remarks are, perhaps, not unnecessary.

The charcoal of gunpowder contains, besides carbon, also oxygen and hydrogen, ash and moisture. The oxygen of the charcoal is, as has already been proved before (p. 544), eliminated with some of the hydrogen as water. The rest of the hydrogen of the charcoal with nitrogen, carbon, and sulphur respectively, forms by-products, the total weight of which, as a rule, does not exceed 2 per cent. of the powder burnt.

The products of combustion, with the exception of those prepared by NOBLE and ABEL, contain always some unburnt carbon and sulphur, and frequently undecomposed saltpetre.

Hence we have :

    a. Chief products: K_2CO_3, K_2SO_4, K_2S_2, CO_2, CO, and N_2.
    b. By-products: H_2, H_2S, CH_4, NH_3, H_2O, and $KCNS$.
    c. Constituents of powder, not burnt: KNO_3, C, and S.

Equation (VIII.) enables us to calculate, from that portion of the powder which produces the chief products (mentioned under *a*), the quantities of these products formed during complete combustion.

We will now proceed to prove, by examples, the correctness of this equation.

BUNSEN and SCHISCHKOFF found in 1 grm. of sporting powder, and in the products of its combustion, the following quantities :—

1 grm. of powder—

Saltpetre	0·7899
Sulphur	0·0984
Charcoal—	
Carbon	0·0769
Hydrogen	0·0041
Oxygen	0·0307

Chief products of combustion—

Potassic sulphate	0·4227
,, carbonate	0·1264
,, hyposulphite . . .	0·0327
,, sulphide	0·0213
Carbonic acid*	0·2159
,, oxide	0·0094
Nitrogen	0·0998
	0·9282

By-products—

|	
Potassic sulphocyanate. . .	0·0030
Hydrogen	0·0002
Sulphuretted hydrogen . .	0·0018
Oxygen	0·0014
Ammonia and water . . .	0·0139
	0·0203

Powder constituents not decomposed or burnt—

Saltpetre	0·0372
Carbon	0·0073
Sulphur	0·0014
	0·0459

Hence—

|	
Chief products	0·9282
By-products	0·0203
Unburnt powder. . . .	0·0459
	0·9944

* Inclusive of the carbonic acid of the ammonic carbonate.

If the potassic hyposulphite is replaced by its equivalent of potassic disulphide, the quantities of the chief products expressed in molecular weights, and calculated for 16 mols. of decomposed saltpetre, we obtain:

$$1\cdot97K_2CO_3 + 5\cdot25K_2SO_4 + 0\cdot45K_2S_2 + 10\cdot59CO_2 + 7\cdot7N_2 + 0\cdot33K_2S + 0\cdot71CO.$$
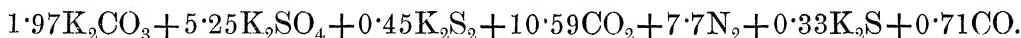
From these symbols we calculate the following composition of the powder:

$$16KNO_3 + 13\cdot2C + 6\cdot48S + 0\cdot66O.$$
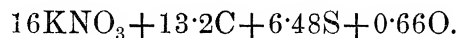
If now we substitute, in equation (VIII.), for x the number 16, for y 13·2, for z 6·5, and for a 0·71, we find for the chief products:

$$2\cdot25K_2CO_3 + 5\cdot01K_2SO_4 + 0\cdot74K_2S_2 + 10\cdot25CO_2 + 0\cdot70CO + 8N_2$$

numbers which closely agree with those found by experiment.

The powder used by BUNSEN and SCHISCHKOFF contains, according to analysis:

$$16KNO_3 + 13\cdot3C + 6\cdot3S$$
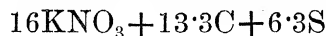
a composition which is nearly the same as that deduced from the chief products of combustion.

The analytical method in this case causes no appreciable error in the determination of the potassic sulphate. Neither, according to my own analysis, does potassic monosulphide, nor, according to NOBLE and ABEL's analysis of the residues of mining powder, does potassic disulphide produce potassic sulphate by treatment with cupric oxide. BUNSEN and SCHISCHKOFF's residues contained a mixture of mono- and disulphide, and of both only a comparatively small quantity.

LINCK* examined the products of combustion of the Würtemberg service powder according to the method employed by BUNSEN and SCHISCHKOFF. He obtained the following results:—

Composition of the powder—

Saltpetre	0·7470
Sulphur	0·1245
Charcoal—	
Carbon	0·0905
Hydrogen	0·0041
Oxygen	0·0278
Water	0·0060
	0·9999

* Ann. der Chemie und Pharm., Bd. cix., p. 53.

Chief products of combustion—

Potassic sulphate	0·2891
„ carbonate	0·1537
„ hyposulphite . . .	0·0374
„ disulphide	0·0959
Carbonic acid*	0·2345
„ oxide	0·0118
Nitrogen	0·0952
	0·9176

By-products—

Potassic sulphocyanate . .	0·0116
Sulphuretted hydrogen . .	0·0238
Hydrogen	0·0003
Oxygen	0·0001
Ammonia and water . . .	0·0098
	0·0456

Powder constituents not decomposed or burnt—

Saltpetre	0·0120
Carbon	0·0183
Sulphur	0·0031
	0·0334

Hence—

|	
Chief products	0·9176
By-products	0·0456
Not burnt	0·0334
	0·9966

If we express the quantities of the chief products by means of molecular weights, and calculate how much of each would be formed by the combustion of a quantity of powder containing 16 mols. of saltpetre, we obtain :

$$2 \cdot 43K_2CO_3 + 3 \cdot 64K_2SO_4 + 0 \cdot 43K_2S_2O_3 + 1 \cdot 47K_2S_2 + 11 \cdot 71CO_2 + 0 \cdot 92CO + 14 \cdot 94N$$
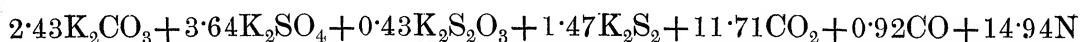
and expressed in powder constituents :

$$16KNO_3 + 15 \cdot 06C + 7 \cdot 44S - 1 \cdot 06N - 0 \cdot 52O.$$
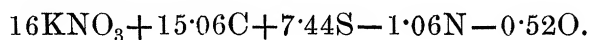
The powder contained, according to analysis :

$$16KNO_3 + 16 \cdot 3C + 8 \cdot 4S.$$
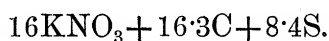
* Inclusive of the carbonic acid in the ammonic carbonate.

The by-products contain no oxygen of the saltpetre, and with the exception of the potassium and nitrogen in the potassic sulphocyanate, and the nitrogen of the ammonia, their elements are derived from the charcoal and sulphur. The chief products should, accordingly, contain all the oxygen of the decomposed saltpetre. This, however, is not the case; 0·52 of an atom is wanting, and if the potassic hyposulphite, as we must assume, has been formed by the oxidising action of the cupric oxide upon the potassic disulphide, then no less than 1·81 atoms or nearly $\frac{1}{26}$th of the oxygen of the decomposed saltpetre have disappeared. LINCK himself finds in the products of combustion 1·75 per cent. or about $\frac{1}{22}$nd less oxygen than in the original powder, and this loss of oxygen would have appeared still greater if he had not assumed that the oxygen of the hyposulphite had been derived from the saltpetre. On the other hand, LINCK finds in the products of explosion 0·71 per cent. or $\frac{1}{12}$th to $\frac{1}{13}$th more of carbon, and 0·9 or $\frac{1}{13}$th to $\frac{1}{14}$th more of sulphur than in the original powder. Accordingly, it follows, either that LINCK's powder has not the composition which he ascribes to it, or that some considerable errors attach to the analytical data of the products of explosion. Hence, no near agreement can here be expected between theory and experiment.

If we replace the potassic hyposulphite found, by its equivalent of potassic disulphide, express the quantity of the chief products by molecular weights, and calculate the composition of that portion of the powder which was transformed into the chief products, we obtain

$$16KNO_3 + 15\cdot06C + 7\cdot44S - 1\cdot06N - 1\cdot81O.$$
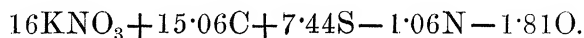
and if in equation (VIII.) we place,

$$x = 16 \qquad\qquad y = 15$$
$$z = 7\cdot5 \qquad\qquad a = 1\cdot0$$

we find the following theoretical values, which are placed by the side of the experimental numbers

			Theory.	Experiment.
	K_2CO_3 . . .		2·14	2·43
$16KNO_3$	K_2SO_4 . . .		4·21	3·64
$15C$ $=$	K_2S_2		1·64	1·90
$7\cdot5S$	CO_2 . . .		11·85	11·71
	CO		1·0	0·92

Some mistake appears to have occurred in the determination of the potassic sulphate and carbonate. The calculation could likewise be carried out in the following manner: The unburnt portion of the powder, and the quantities of the elements contained in the by-products, could be subtracted from the composition of the quantity of powder taken for experiment, and from the rest, the quantities of the products might be

calculated according to equation (VIII.). This mode of calculation is in LINCK's case not applicable, because large quantities of charcoal remained unburnt, the composition of which is not known. This charcoal having been exposed to the high temperature developed by the combustion of the powder can no longer have had the original composition, but was probably nearly pure carbon.

The composition of the Austrian cannon powder can be represented by the symbols :

$$16KNO_3 + 19 \cdot 8C + 8 \cdot 7S$$
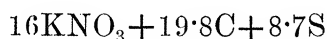
if hydrogen, oxygen, ash, and moisture of the charcoal are neglected. All the potassium and the oxygen of the decomposed saltpetre reappeared in the chief products of explosion, but more than 4 atoms of carbon and 3 atoms of sulphur remained free. The amount of the sulphide formed by this powder was very small in KAROLYI's experiment.

The powder constituents which were transformed into the chief products are represented by the symbols

$$16KNO_3 + 14 \cdot 32C + 5 \cdot 28S$$
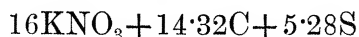
and 2·04 mols. of CO had been formed (p. 549).

The values of these coefficients substituted for x, y and z in equation (VIII.) yield the following theoretical quantities of the chief products of combustion, to which are appended the quantities found by experiment :—

		Theory.	Experiments.
K_2CO_3	. . .	3·06	3·05
K_2SO_4	. . .	4·59	4·61
K_2S_2	. . . .	0·33	0·33
CO_2	. . . .	9·12	9·23
CO.	. . . .	2·04	2·04
N_2.	. . . .	8·0	7·55

$$\left. \begin{array}{l} 16KNO_3 \\ 14 \cdot 32C \\ 5 \cdot 24S \end{array} \right\} =$$

a striking confirmation of theory is thus presented.

The analysis of the products of explosion of rifle powder carried out by KAROLYI is contaminated by a considerable error. He finds, correctly, no oxygen in the by-products ; but no less than 4 atoms or $\frac{1}{12}$th more oxygen appears in the chief products than in the decomposed saltpetre, and if from this the oxygen of the charcoal be subtracted there remain still 1·66 atoms of oxygen more than were contained in the entire powder. If these errors of experiment are corrected, by means of equation (VII.), a very good agreement of the numbers calculated according to equation (VIII.), and those derived from experiment, is obtained for rifle powder.

The mean composition of the powders of Waltham Abbey is expressed by the symbols

$$16KNO_3 + 21 \cdot 18C + 6 \cdot 63S$$
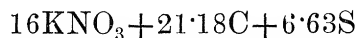
and because, during their combustion, 0·67 mol. of sulphuretted hydrogen is formed, there remain

$$16KNO_3 + 21 \cdot 18C + 5 \cdot 96S$$
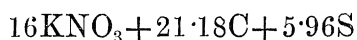
for the formation of the principal products.

But as the portion of the sulphur which has united with the iron of the apparatus has not been determined by direct experiment, we are obliged to form an estimate of its amount from other considerations.

According to the remarks on pages 557–559, potassium disulphide is produced by the metamorphosis of gunpowder. The combustion of a quantity of powder containing 16 mols. of saltpetre produces, if we take the mean of all the experiments of NOBLE and ABEL, 0·90 mol. of K_2SO_4 and 2·1 mols. of K_2S_2, for which quantities 1 mol. of K_2SO_4 and 2 mols. of K_2S_2 have been placed in equation (II.). From this it follows that 5 atoms of sulphur have taken part in the metamorphosis, and that 0·96 atom of sulphur has remained free or has united with the iron of the explosion apparatus.

The experiments of KAROLYI support this conclusion. The Austrian cannon powder containing 8·7 atoms, and the rifle powder 5·66 atoms of sulphur for every 16 mols. of saltpetre, and in the principal products of combustion of the former 5·25 atoms, and in those of the latter 4·89 atoms of this element were found, the rest of the sulphur having remained free. In spite of the great difference of the amounts of sulphur in the two descriptions of powders, we find in their products of combustion, for 16 mols. of decomposed saltpetre, almost the same quantity of sulphur, 5 atoms, in both cases. In NOBLE and ABEL's experiments the sum of the sulphur in the sulphate and disulphide is likewise equal to 5 atoms. From this equality we may conclude that in NOBLE and ABEL's, as in KAROLYI's experiments, during the first stage of combustion, or the stage of explosion, the powders were transformed according to equation (IV.), page 553, and that 5 of the 5·96 atoms of sulphur entered into combination. The remaining 0·96S should, during the second stage, have reacted with potassic carbonate according to equation (V.), page 559, but as this reaction appears not to have occurred, we may conclude, with great probability, that the 0·96 atom of sulphur united with the metal of the apparatus.

Since in NOBLE and ABEL's experiments all the powder introduced into their apparatus was completely burnt, and as the sum of the weights of the secondary products, after deducting the sulphuretted hydrogen, is very small, and finally, because potassium, oxygen, and carbon in the principal products of combustion occur almost in the same proportions as in the saltpetre and charcoal of the original powder, we can substitute for x and y, in equation (VIII.), the values derived directly from the composition of the powder,

If then we put in equation (VIII.) $x=16$, $y=21\cdot18$, $z=5$, and for a, the carbonic oxide, the number $3\cdot23$, found by experiment, we obtain for the principal products values which in the following table have been placed by the side of those found by experiment :—

		Theory.	Experiment.
	K_2CO_3	5·01	4·98
	K_2SO_4	0·96	0·90
$16KNO_3$ $+21\cdot18C$ $+5S$	K_2S_2	2·01	2·10
	CO_2	12·93	13·13
	CO	3·23	3·23
	N_2	8·00	8·67

The theoretical numbers agree in a very satisfactory manner with those found by experiment.

According to what has been stated in these pages, we conceive the metamorphosis of gunpowder to take place in a shell, or in the bore of a gun, in the following manner. In the first moments after ignition, during the explosion, powders of different composition burn according to the equation

$$16KNO_3+13C+5S=3K_2CO_3+5K_2SO_4+9CO_2+CO+8N_2$$
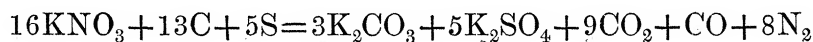
and in case of a shell which will burst almost immediately and its contents be scattered about, no further changes take place.

In the bore of a gun the gases expand, move the shot, and by the performance of this work lose a portion of their energy; the products of the first stage of the metamorphosis, potassic carbonate and potassic sulphate, remain at a red heat, in a fluid condition, for a longer time in contact with free carbon and sulphur, and produce, according to equations (V.) and (VI.), an additional quantity of carbonic acid. This carbonic acid, which is generated during the movement of the shot in the bore, prevents the too rapid diminution of the tension of the gases; the heat of the solid products is, in part, transformed into *vis viva* of the gas molecules. If the gun were long enough and the quantities of carbon and sulphur not too large, every atom of the former might be oxidised by the oxygen of the potassic sulphate, and the entire amount of the sulphur be converted into potassic disulphide and sulphate by contact with potassic carbonate. But in reality this second stage of the metamorphosis is perhaps never complete; the shot will have left the gun before the termination of these comparatively slow reactions.

The mining powders, strictly considered, do not belong to the category of gun-powders; they contain a large excess of carbon and sulphur. But as their metamorphosis clearly shows the source of the by-products of the combustion of gunpowder, we will discuss here the analytical data furnished by NOBLE and ABEL of an experiment with a sample obtained from CURTIS and HARVEY.
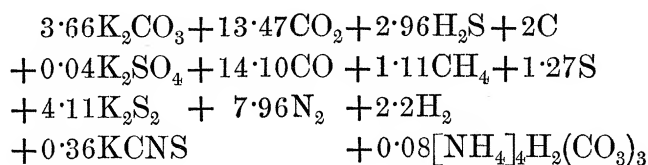
COMPOSITION of the powder

Saltpetre	. . . .	61·66
Sulphur	. . . .	15·05
Charcoal { Carbon	. . . .	17·93
Hydrogen	. . . .	0·66
Oxygen	. . . .	2·23
Water	. . . .	1·66
		99·19

which may be represented by the symbols:

$$16KNO_3 + 12\cdot3S + \underbrace{39\cdot18C + 16\cdot16H + 3\cdot65O}_{\text{charcoal.}}$$
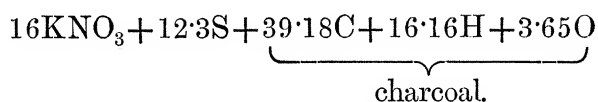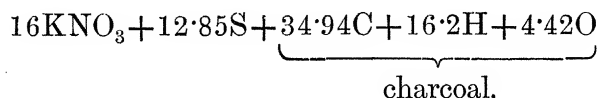
This mixture contains sulphur and carbon nearly in the same proportions as they occur in the service powder of Waltham Abbey [S : C = 1 : 3·21], and therefore differs by containing much less saltpetre.

The products of combustion, calculated for 16 mols. of decomposed saltpetre, yielded the following results :—

$$3\cdot66K_2CO_3 + 13\cdot47CO_2 + 2\cdot96H_2S + 2C$$
$$+ 0\cdot04K_2SO_4 + 14\cdot10CO + 1\cdot11CH_4 + 1\cdot27S$$
$$+ 4\cdot11K_2S_2 \quad + 7\cdot96N_2 \quad + 2\cdot2H_2$$
$$+ 0\cdot36KCNS \qquad\qquad + 0\cdot08[NH_4]_4H_2(CO_3)_3$$

from which we calculate the composition of the powder as follows :—

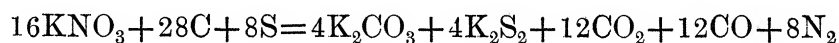$$16KNO_3 + 12\cdot85S + \underbrace{34\cdot94C + 16\cdot2H + 4\cdot42O}_{\text{charcoal.}}$$

If we contrast the above results with those obtained by the explosion of the service powders of Waltham Abbey, (I.), page 545, it is seen that the large excess of carbon and sulphur in the mining powder has not diminished the amount of carbonic acid, but greatly increased the quantity of carbonic oxide. In the service powders, the oxygen of the charcoal is eliminated, with hydrogen, as water; in the mining powder it is found at the end of the combustion in union with carbon as carbonic oxide. The hydrogen of the charcoal thus set free partly remains so, partly unites with carbon and nitrogen respectively, forming marsh gas and ammonia, and during the cooling of the products, at a lower temperature, gives rise to the generation of much sulphuretted hydrogen.

In consequence of the great excess of charcoal and sulphur, carbonic oxide, marsh gas and sulphuretted hydrogen are, calculated for 16 mols. of decomposed saltpetre,
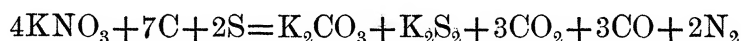
from four to five times greater in the products of the mining powder than in those of the service powder. The gases of the former are combustible, those of the latter are not.

The potassic sulphocyanate has been formed by the metamorphosis of CURTIS and HARVEY's powder in quantities ten times as large as were observed amongst the products of the Waltham Abbey mixtures. It is well known that potassic carbonate, sulphur and charcoal, at a white heat, in an atmosphere containing nitrogen, will produce potassic sulphocyanate. The amount of potassic sulphate, as might be expected, present among the products of the mining powder is almost *nil*, and the source of the by-products of the combustion of gunpowder is laid bare.

If we discard the by-products, we obtain for the combustion of a powder with an excess of carbon the equation :

$$16KNO_3 + 28C + 8S = 4K_2CO_3 + 4K_2S_2 + 12CO_2 + 12CO + 8N_2$$

or more simply :

$$4KNO_3 + 7C + 2S = K_2CO_3 + K_2S_2 + 3CO_2 + 3CO + 2N_2$$

which represents with sufficient exactness the reactions between saltpetre, carbon, and sulphur, when an excess of carbon is present and is introduced in the form of charcoal. Carbonic acid and oxide have been found by experiment to be a little higher, in consequence of the action of the oxygen of the charcoal, potassic carbonate a little lower, in consequence of the formation of some potassic sulphocyanate, than is required by the foregoing equation.

It is also worthy of notice that in spite of the presence of free carbon, more than 13 mols. of CO_2 have remained undecomposed.

From the remarks of the preceding pages it follows that during the complete metamorphosis of powder, the reactions between the constituents of saltpetre, the carbon of the charcoal, and sulphur, take place according to equations (III.), (IV.), (V.), (VI.), and (VII.), and that by means of equation (VIII.) the products, namely, potassic carbonate, potassic sulphate, potassic disulphide, carbonic acid and nitrogen, which are formed during the combustion of a weight of powder containing x mols. of saltpetre, y atoms of carbon, and z atoms of sulphur, can be calculated in a satisfactory manner. It now remains to calculate, by means of the same equation, the quantities of heat, gas, and energy which powders of various composition are able to produce.

For this purpose we assume that we have to deal with mixtures of saltpetre, sulphur, and pure *carbon*, and that the combustion is complete, viz.: that it runs to the end of the second stage. If we conceive that during the transformation of the powder no carbonic oxide is formed, we should, as a consequence, have a considerable simplification of equation (VIII.) without influencing much the calculated amounts of gas and heat.

The conversion of the carbonic oxide to carbonic acid could only take place at the expense of the oxygen in the potassic sulphate; if it occurred according to the equation

$$K_2SO_4 + 4CO = K_2S + 4CO_2$$
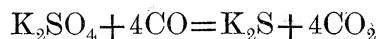
the volume of the gas would not be changed. But since potassic disulphide is formed, we have to base our calculations on equation

$$2K_2SO_4 + 7CO = K_2CO_3 + K_2S_2 + 6CO_2$$

from which it follows that, if no carbonic oxide but only carbonic acid is produced, the volume of the entire gas will be diminished by $\frac{1}{7}$th of the volume of the carbonic oxide which in reality is formed.

The greatest amount of carbon in gunpowders generally, as far as I know, is contained in the mixtures of Waltham Abbey, and these also produce the largest quantity of carbonic oxide, 3 mols. or 6 vols. for every 16 mols. of decomposed saltpetre. In addition to 3 mols. of carbonic oxide, 13 mols. of carbonic acid and 8 mols. of nitrogen are generated, which together amount to 24 mols. or 48 vols. of gas.

Now, if in place of carbonic oxide, carbonic acid had been formed, the volume of the entire gas would have been 47·14 instead of 48 vols. In other words, if we frame our calculation on the assumption that only carbonic acid and no oxide has resulted from the combustion, we shall find for the English service powders 1·8 per cent. less gas than was actually obtained by experiment. And as other descriptions of powder contain less carbon than those of Waltham Abbey, in their case the error will be smaller than 1·8 per cent. If then we calculate the volumes of gas which mixtures of saltpetre, carbon, and sulphur in various proportions will produce, on the assumption that no carbonic oxide, but only carbonic acid is formed, we shall obtain numbers that will not differ much from the sum of the volumes of carbonic acid, carbonic oxide, and nitrogen produced by gunpowders containing corresponding quantities of saltpetre, carbon, and sulphur.

By adding the coefficients of carbonic acid and nitrogen of equation (VIII.), and putting $x = 16$, and $a = 0$, we obtain for the sum, G, of the molecules of carbonic acid and nitrogen, which a mixture of 16 mols. of saltpetre, y atoms of carbon, and z atoms of sulphur, by its complete combustion, can produce, the equation

$$G = \frac{160 + 20y + 16z}{28}$$

and for the volume, V

$$V = \frac{160 + 20y + 16z}{14} \qquad . \qquad . \qquad . \qquad . \qquad . \qquad . \qquad . \quad \text{(IX.)}$$

In Bunsen and Schischkoff's experiment 16 mols. of saltpetre, 13·3 atoms of carbon, and 6·3 atoms of sulphur were consumed in the formation of the chief products of combustion (page 562). The values $y = 13·3$, $z = 6·3$, placed in equation (IX.), give $V = 37·62$. Now 16 mols. of saltpetre, 13·3 atoms of carbon, and 6·3 atoms of sulphur correspond to 1977·2 parts by weight, and if these parts are expressed in grammes, then

1 vol. of gas will be equal to 11·19 litres, and 37·62 vols.=420967·8 cub. centims. Hence, 1 grm. of the powder would produce 212·9 cub. centims. of gas.

But only 92·8 per cent. of the powder was transformed, according to equation (VIII.), therefore

$$\frac{212\cdot9 \times 92\cdot8}{100} = 197\cdot5 \text{ cub. centims.}$$

BUNSEN and SCHISCHKOFF found 193·1 cub. centims. If we deduct from this number 4·5 cub. centims., the volume of the gaseous by-products, hydrogen, sulphuretted hydrogen, and oxygen, and add 7·4 cub. centims. for the carbonic acid of the ammonic carbonate, we obtain 196 cub. centims. for the gas found by experiment.

Hence :

Experiment.	Theory.
196 cub. centims.	197·5 cub. centims.

The chief products of the combustion of LINCK's powder contain, according to his analysis, the powder constituents in the proportion

$$16KNO_3 + 15\cdot06C + 7\cdot44S.$$
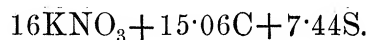
If we substitute in equation (IX.) for y the number 15, and for z 7·5, we obtain V=41·42. $16KNO_3 + 15C + 7\cdot5S$ corresponds to 2036 parts by weight. Expressed in grammes 1 vol. of the gas will be equal to 11190 cub. centims., therefore 41·42 vols. =463489·8 cub. centims., and 1 grm. of the powder would yield 227·6 cub. centims.

As only 91·7 per cent. of the Würtemberg service powder was transformed, according to equation (VIII.), we have

$$\frac{227\cdot6 \times 91\cdot7}{100} = 208\cdot7 \text{ cub. centims. for the theoretical volume.}$$

LINCK found 218·35 cub. centims.; but from this must be subtracted 15·67 cub. centims. for sulphuretted hydrogen, 3·56 cub. centims. for hydrogen, and 0·09 for oxygen, leaving 199·3 cub. centims. of gas as the product of combustion of 1 grm. of powder according to equation (VIII.). Adding 5·8 cub. centims. for carbonic acid in ammonic carbonate, we obtain

Experiment.	Theory.
205·1 cub. centims.	208·7 cub. centims.

If the difficulties which have to be overcome in order to obtain exact results in the determination of the products of explosion of gunpowder are considered, the differences between the theoretical and experimental numbers appear to come within the errors of observation.

In NOBLE and ABEL's experiments 16 mols. of saltpetre, 21·35 atoms of carbon,

and 5·1 atoms of sulphur were transformed according to equation (VIII.).   If in equation (IX.) for y the number 21·35, and for z the number 5·1 is substituted, the volume of gas is found to be 47·73.

16KNO$_3$+21·35C+5·1S are equal to 2035·4 parts by weight, and 47·73 vols.= 534098·7 cub. centims., if the weight is expressed in grammes, therefore : 1 grm. of the powder yields 262·4 cub. centims. of gas.

On an average, 93·75 per cent. of the weight of the powder was transformed, according to equation (VIII.), hence we have :

$$\frac{262 \cdot 4 \times 93 \cdot 75}{100} = 246 \cdot 0 \text{ cub. centims.}$$

for the theoretical volume of gas formed by the combustion of 1 grm. of powder. The mean of NOBLE and ABEL's observations is 268·7 cub. centims.   From this number 14·5 cub. centims. must be subtracted for the volumes of sulphuretted hydrogen, marsh gas, and hydrogen, leaving 254·2 cub. centims. for the carbonic acid, carbonic oxide, and nitrogen.   Therefore we obtain, for the volume of the gas produced by 1 grm. of service powder from Waltham Abbey,

Experiment.	Theory.
254·2 cub. centims.	246 cub. centims.

the difference between the two numbers is only 1·9 cub. centim. greater than the greatest difference between two observations made with R. L. G. powder.

The three descriptions of powder, BUNSEN and SCHISCHKOFF's, LINCK's, and NOBLE and ABEL's, contain from 13 to 21 atoms of carbon, and from 6·3 to 8·4 atoms of sulphur for every 16 mols. of saltpetre, and are good representatives of gunpowder in general.

The values calculated for the volumes of the gases furnished by these powders are near enough to those found by experiment to show the correctness of the theoretical considerations on which equation (IX.) has been framed, and to justify the use of this equation for the determination of the volume of gas produced by mixtures which contain saltpetre, carbon, and sulphur in proportions different from those of the Waltham Abbey, the Würtemberg, or BUNSEN and SCHISCHKOFF's powder.

The amount of heat generated by the combustion of a mixture of saltpetre, *pure* carbon, and sulphur can be found in the following manner :

If we assume, as in the case of the calculation of the gas, that no carbonic oxide is formed, that is to say put $a = 0$, multiply the heat of formation of each product with its coefficient in equation (VIII.), add the products thus formed and subtract from the sum the heat of formation of saltpetre : the difference will be equal to the heat generated by the combustion of the mixture.

$$\text{Heat of formation of 1 mol. } K_2CO_3 = 279530^*$$
$$\text{,,} \qquad \text{,,} \qquad \text{,,} \quad K_2SO_4 = 344640\dagger$$
$$\text{,,} \qquad \text{,,} \qquad \text{,,} \quad K_2S_2 \ = 108000\ddagger$$
$$\text{,,} \qquad \text{,,} \qquad \text{,,} \quad CO_2 \ = 97000\S$$
$$\text{,,} \qquad \text{,,} \qquad \text{,,} \quad KNO_3 = 119480\|$$

Hence we obtain for the heat of combustion, W

$$[\tfrac{4}{28}x + \tfrac{8}{28}y - \tfrac{16}{28}z]279530 + [\tfrac{20}{28}x - \tfrac{16}{28}y + \tfrac{4}{28}z]344640$$
$$+ [-\tfrac{10}{28}x + \tfrac{8}{28}y + \tfrac{12}{28}z]108000 + [-\tfrac{4}{28}x + \tfrac{20}{28}y + \tfrac{16}{28}z]97000$$
$$-x \times 119480 = W \text{ ; or if } x = 16,$$
$$W = 1000[1827 \cdot 154 - 16 \cdot 925y - 8 \cdot 788z] \ . \ . \ . \ . \ . \ . \ . \ . \quad \text{(X.)}$$

That is to say, a mixture of 16 mols. of saltpetre, y atoms of carbon, and z atoms of sulphur, will, by its complete transformation according to equation (VIII.), produce W units of heat.

An error attaches to W in consequence of the assumed non-formation of carbonic oxide.

The quantity of this substance produced by the Waltham Abbey powders is greater than that formed by other mixtures, but as the error attaching to W in the case of the English service powders does not amount to more than 2·6 per cent. of the total heat, an error smaller than the usual errors of observation, it may be neglected for the sake of the great simplification of the formula.

It is perhaps desirable again to call attention to the condition that the equations (IX.) and (X.) apply only to mixtures which contain their constituents in such proportions that they can completely transform themselves according to equation (VIII.). Mining powders are excluded.

The charcoal of gunpowder is, however, not pure carbon, but contains also hydrogen, oxygen, and water.

The high temperature generated by the explosion causes probably the dissociation of these elements, and if, as in NOBLE and ABEL's experiments, all the carbon is oxidised at the expense of the oxygen of the saltpetre, the oxygen of the charcoal will reunite with hydrogen and form water.

The heat absorbed by the decomposition of the charcoal is not known. A portion of the hydrogen unites with nitrogen, carbon, and sulphur respectively, forming ammonia, marsh gas, and sulphuretted hydrogen. The total heat which is either liberated or absorbed by all these secondary reactions, appears, however, to be a small

* J. THOMSEN, 'Berichte der deutschen Chemischen Gesellschaft in Berlin,' Bd. xii., p. 2031.

† Ibid., p. 2032; Bd. xiii., p. 961.

‡ SABATIER, Comptes Rendus, tom. xc., 1557–1560 ; Chem. Soc. Journal, 1880, p. 689.

§ J. THOMSEN, 'Berichte der deutschen Chemischen Gesellschaft in Berlin,' Bd. xiii., p. 1329.

‖ Ibid., p. 500.

quantity, when compared with the amount given off by the formation of potassic carbonate, potassic sulphate, potassic disulphide, and carbonic acid. The following condition has a greater influence on the heat of combustion of ordinary gunpowder.

The combustion ought to be complete; but in BUNSEN and SCHISCHKOFF's as well as in LINCK's experiments, a not inconsiderable portion of the powder remained unburnt. In every calorimetric determination all the products ought to be carefully examined, and this it seems was not done by those who have determined the heat of combustion of gunpowder. From the foregoing remarks we conclude that no close agreement can be expected between the heat of combustion calculated by means of equation (X.) for a mixture of 16 mols. of KNO_3, y atoms of C, and z atoms of S, and that generated by an ordinary gunpowder containing saltpetre, carbon, and sulphur in the same proportions.

In BUNSEN and SCHISCHKOFF's powder we have for every 16 mols. of saltpetre, 13·3 atoms of C, and 6·3 atoms of S. If we substitute for y the number 13·3 and for z the number 6·3 in equation (X.), we obtain:

$$W = 1546688 \text{ cal.}$$

$16KNO_3 + 13·3C + 6·3S = 1977·2$ parts by weight, or one part of their powder would furnish 782 units of heat. BUNSEN and SCHISCHKOFF found 619·5. This number is, I believe, the result of one experiment made with 0·71 grm. of powder; it is evidently much too small. NOBLE and ABEL found, for the heat of combustion of the powders of Waltham Abbey, values which vary between 696 and 727 units. Their numerous calorimetric determinations were made by the combustion of the powders in the explosion apparatus, and several hundred grammes were used in each experiment. It is known that the combustion under such conditions is complete. But as the English powders contain much more carbon than BUNSEN and SCHISCHKOFF's, or 4 per cent. less of saltpetre, they ought to have produced less heat. From these considerations it seems to follow that in BUNSEN and SCHISCHKOFF's experiment a portion of the powder taken escaped combustion.

It has been shown that 16 mols. of saltpetre, 21 atoms of C, and 5 atoms of S take part in the metamorphosis of the powders of Waltham Abbey. If for y the number 21, for z the number 5, are substituted in equation (X.), the value of W is found to be equal to 1427789 cal.; but $16KNO_3 + 21C + 5S = 2028$ parts by weight, hence 1 grm. of powder would generate 704 units of heat.

NOBLE and ABEL found in the first series, comprising five experiments, numbers which give a mean of 702·34 units for 1 grm. of powder.

In another series of 19 experiments greater numbers were obtained than in the first. The mean of all 24 experiments is equal to 719·9 cal.

The theoretical number of 704 cal., however, corresponds to a mixture of saltpetre, sulphur, and pure carbon.

93·75 per cent. of the English service powders are transformed, according to equation

(VIII.), hence the calculated heat generated by the reactions between saltpetre, sulphur, and pure carbon of 1 grm. of English service powder is :

$$\frac{704 \times 93\cdot75}{100} = 660 \text{ cal.}$$

This theoretical quantity is $59\cdot9$ units, or $8\cdot4$ per cent. less than the amount found by experiment, a difference which would be much smaller if the amount of heat produced by the action of the sulphur upon the iron of the apparatus were known and could be subtracted from the experimental number. It is worthy of notice that the differences in the amounts of heat found in several experiments made with the same description of powder are nearly as great as the differences between the calculated and observed results.

A sample of powder manufactured by CURTIS and HARVEY, and marked No. 6, gave in four experiments

I.	II.	III.	IV.
$732\cdot9$	$744\cdot9$	$755\cdot7$	784

units of heat, hence, between the first and last experiment a difference of $51\cdot1$ units.

Another heat determination may be here introduced. $16KNO_3 + 16\cdot4C + 5\cdot5S$ of the Spanish pebble powder burnt according to the reactions on which equation (VIII.) is based, $16\cdot4$ for y, and $5\cdot5$ for z put in equation (X.), make $W = 1501250$ cal. As

$$16KNO_3 + 16\cdot4C + 5\cdot5S$$
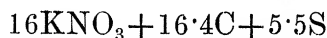
are equal to $1988\cdot8$ parts by weight, 1 grm. of the powder generates 754 cal.

If 5 per cent. are deducted for hydrogen, oxygen, and ash, we obtain :

$$\frac{754 \times 95}{100} = 716\cdot3 \text{ cal.}$$

for the calculated heat of 1 grm. of powder. Experiment gave $762\cdot3$, or 46 units more.

It follows as a general result from these considerations that the mean quantities of heat generated by the combustion of the English service and Spanish pebble powders are about 60 units greater than the theoretical values. If, however, the amount of heat generated by the action of the sulphur upon the iron of the explosion apparatus were known, and could be subtracted from the observed quantities of heat, the difference would become much smaller.

On the other hand, the theoretical numbers stand to each other nearly in the same ratios as do the corresponding experimental values.

The equations (VIII.), (IX.), and (X.) will now be used to determine the composition of an ideal powder, that is to say, of a powder composed of saltpetre, *pure* carbon, and

sulphur, which shall, of all possible mixtures of this nature, possess the greatest energy; the results so obtained will be nearly correct for ordinary gunpowders. This would be the most general form of the problem of the explosion of gunpowder which could be proposed for solution to a chemist.

Equations (IX.) and (X.), viz. :—

$$V = \tfrac{160}{14} + \tfrac{20}{14}y + \tfrac{16}{14}z \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (IX.)$$

$$W = 1000[1827\cdot154 - 16\cdot925y - 8\cdot788z] \quad . \quad . \quad . \quad . \quad . \quad (X.)$$

at once show that, if for a given weight of saltpetre, 16 mols., the carbon and sulphur of the mixture were allowed to increase, the volume of gas generated by combustion would likewise increase, but the quantity of heat will grow smaller, and if the carbon and sulphur be diminished the gas will also become less, but the heat of combustion will increase.

NOBLE and ABEL have called attention to the fact[*] that the products of heat and gas obtained by them in their various experiments with different descriptions of powder do not differ much from each other. The explanation of this interesting observation is to be found in equations (IX.) and (X.).

The work which can be performed by a given weight of powder will, *cæteris paribus,* be proportional to the volume of gas and amount of heat, respectively, which the powder can produce by its combustion, and hence, will be proportional to the product of both. This is, however, only approximately correct, because, if we have to compare the work which two powders of different composition can produce, the gases given off by the one will not contain the elements in the same proportion as those produced by the other; a portion of the energy developed will be consumed in the performance of interior work during the expansion of the carbonic acid. This portion is, however, very small.

The product of (IX.) and (X.) is :

$$10440\cdot88 - 12\cdot09y^2 + 1208\cdot39y - 15\cdot95yz + 993\cdot867z - 5\cdot022z^2 = \frac{W.V}{1000 \times 2} = E \quad . \qquad (XI.)$$

the factor 1000 in (X.) has been omitted, or W divided by 1000, and V by division by 2 has been converted from volumes into molecules.

The equations (IX.) and (X.) are based on the assumption that no carbonic oxide is formed during the combustion of a mixture of saltpetre, carbon, and sulphur. In consequence, the volume of gas calculated by formula (IX.) for a mixture of the composition like those of Waltham Abbey is 1·8 per cent. smaller, and the amount of heat

* Phil. Trans., 1880, p. 230.

according to equation (X.) 2·6 per cent. larger than it would have been if the carbonic oxide had been taken into consideration. These errors nearly compensate each other in the product E in the equation (XI.), so that the values of E are but *little* affected by putting a, the carbonic oxide, $=0$ in equation (VIII.).

Equation (XI.) can be used for the calculation of the relative energies of weights of powder containing 16 mols. of saltpetre, y atoms of carbon, and z atoms of sulphur.

The question now arises for what values of y and z will E in equation (XI.) assume a maximum value, provided that y and z render the coefficients of equation (VIII.) positive,—the condition which must be fulfilled in a chemical equation.

If we put $a=0$ in equation (VIII.), we obtain :

$$\left. \begin{array}{c} x\mathrm{KNO_3} \\ +y\mathrm{C} \\ +z\mathrm{S} \end{array} \right\} = \left\{ \begin{array}{l} \tfrac{1}{28}[\quad 4x+\ 8y-16z](\mathrm{K_2CO_3}) \\ +\tfrac{1}{28}[\quad 20x-16y+\ 4z](\mathrm{K_2SO_4}) \\ +\tfrac{1}{28}[-10x+\ 8y+12z](\mathrm{K_2S_2}) \\ +\tfrac{1}{28}[-\ 4x+20y+16z](\mathrm{CO_2}) \\ +\tfrac{1}{2}x\mathrm{N_2} \end{array} \right. \quad \ldots \ldots \text{(XII.)}$$

in which, as in (VIII.), x, y, and z denote positive numbers. Let a rectangular coordinate system be given with its origin in point A, and the coordinates of a point P be represented by x, y, and z. The coefficients of potassic carbonate, sulphate, and disulphide in (XII.) will for certain values of x, y, and z be equal to 0. The equations :

$$4x+\ 8y-16z=0$$
$$20x-16y+\ 4z=0$$
$$-10x+\ 8y+12z=0$$

satisfied by these values represent three planes which form a trihedral angle with its vertex in the origin and one edge in the $x\,\mathrm{A}\,y$ plane. The points within the trihedral angle have coordinates which will render all the coefficients of (XII.) positive, those situated outside give values for x, y, and z, which will make at least one of the three coefficients of the potassium salts negative. Hence, coordinates of the points within the trihedral angle denote quantities of saltpetre, carbon, and sulphur, which can transform themselves completely into potassic carbonate, sulphate, disulphide, carbonic acid, and nitrogen, whereas the points outside represent, by their coordinates, quantities of the powder constituents which cannot do so entirely, because one or the other of these constituents is in excess or defect.

The points on the faces of the trihedral angle correspond to mixtures which will burn with the production of two, those on the edges with only one of the three potassium salts.

But to show the connexion between the quantities of the constituents of a given powder and those of its products of combustion, we need only consider relative, and not absolute quantities.

If a straight line be drawn through the origin within the trihedral angle the ratios of the coordinates of every point upon it will be the same.

A plane at right angles to the x axis will cut the faces of the trihedral angle so as to form a triangle B D C (see fig. 1), and the coordinates of the points inside this triangle will represent all possible proportions of carbon and sulphur which can with a given weight of saltpetre transform themselves into the products of combustion indicated in equation (XII.). If then in (XII.) we attribute to x the constant value 16, we obtain :

$$16KNO_3 \atop +yC \atop +zS \Biggr\} = \begin{cases} \frac{1}{28}[\quad 64 + 8y - 16z](K_2CO_3) \\ +\frac{1}{28}[\quad 320 - 16y + 4z](K_2SO_4) \\ +\frac{1}{28}[-160 + 8y + 12z](K_2S_2) \quad . \quad . \quad . \\ +\frac{1}{28}[-\ 64 + 20y + 16z](CO_2) \\ +8N_2 \end{cases} \quad \text{(XIII.)}$$

and from it the equations :

$$64 + 8y - 16z = 0 . \quad . \quad . \quad . \quad . \quad . \quad . \quad \text{(XIV.)}$$

$$320 - 16y + 4z = 0 . \quad . \quad . \quad . \quad . \quad . \quad . \quad \text{(XV.)}$$

$$-160 + 8y + 12z = 0 . \quad . \quad . \quad . \quad . \quad . \quad . \quad \text{(XVI.)}$$

of the lines of intersection of the plane at right angles to the x axis with the faces of the trihedral angle, in other words, the sides of the triangle B D C (fig. 1).

Fig. 1.
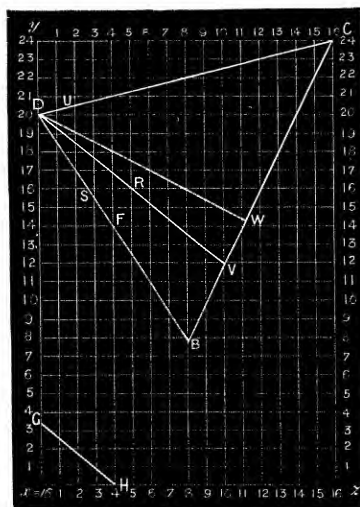
It will be observed that

(XIV.) is the equation of B C
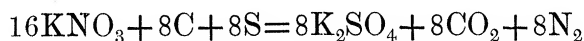(XV.)   „   „   D C
(XVI.)   „   „   B D.

The points of the side B C represent, by their coordinates, mixtures of carbon and sulphur with 16 mols. of saltpetre, which will by complete combustion produce no potassic carbonate; those of side D C such as will not form potassic sulphate, and finally, the coordinates of the points of side B D denote quantities of carbon and sulphur which will burn with 16 mols. of saltpetre without the formation of potassic disulphide. The coefficient of carbonic acid will never vanish, but be always positive, because if it is equated to zero it will represent the line G H in figure, which does not intersect the triangle B D C.

All points outside the triangle B D C have coordinates which render at least one of the three coefficients of the potassium salts in equation (XIII.) negative, and consequently have reference to mixtures of carbon and sulphur with 16 mols. of saltpetre, which contain either too much or too little of one or both of the two elements named.

The coordinates of the line B D represent mixtures of carbon and sulphur with 16 mols. of saltpetre, which will burn without the formation of potassic disulphide, and those of the line B C, such as will not produce potassic carbonate; hence, it may be concluded that the coordinates of B, the point of intersection of the two lines will correspond to a powder which will be transformed without formation of potassic carbonate and disulphide, and will only yield, as products of its combustion, potassic sulphate, carbonic acid, and nitrogen. The coordinates of point B are:

$$y = 8$$
$$z = 8$$

and these values substituted in equation (XIII.).

$$16KNO_3 + 8C + 8S = 8K_2SO_4 + 8CO_2 + 8N_2$$

or simplified:
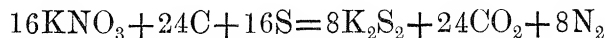
$$2KNO_3 + C + S = K_2SO_4 + CO_2 + N_2$$
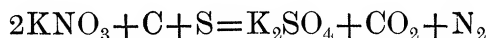
Accordingly a mixture of 82·1 parts of saltpetre, 4·8 parts pure carbon, and 13 parts of sulphur may be expected to produce during complete combustion only potassic sulphate, carbonic acid, and nitrogen, and this conclusion is in perfect accord with the thermochemical relations of the reacting substances and with experimental results. And by a similar method of reasoning we arrive at the conclusion that the coordinates of the point D represent a mixture which will burn according to the equation:
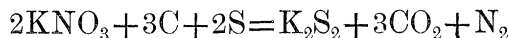
$$16KNO_3 + 20C = 8K_2CO_3 + 12CO_2 + 8N_2$$

or simplified :

$$4KNO_3 + 5C = 2K_2CO_3 + 3CO_2 + 2N_2$$
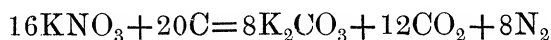
and those of point C according to

$$16KNO_3 + 24C + 16S = 8K_2S_2 + 24CO_2 + 8N_2$$

or simplified :

$$2KNO_3 + 3C + 2S = K_2S_2 + 3CO_2 + N_2$$

if in this last equation the potassic disulphide be changed into monosulphide, then the equation would become identical with the old one, which for many years was supposed to represent the metamorphosis of all sorts of gunpowders.

As already observed, all points within the triangle represent, by their coordinates, mixtures of carbon and sulphur with 16 mols. of KNO_3, which besides carbonic acid and nitrogen, will yield during their combustion three potassium salts.

The geometrical construction of the coefficients of equation (XIII.), does not only offer the advantage of representing by the coordinates of the points within the triangle B D C all possible proportions of saltpetre, carbon, and sulphur which can transform themselves into potassic carbonate, potassic sulphate, potassic disulphide, carbonic acid and nitrogen, but it also enables us to deduce at once, geometrically, the quantities of these products of combustion.

If we desire to know the composition of all those mixtures which shall contain variable quantities of carbon and sulphur, but shall all produce by their combustion the same amount of potassic carbonate, we can deduce the answer from the following considerations :

For such mixtures the coefficient of the potassic carbonate in equation (XIII.) must assume a constant value.   Hence,

$$64 + 8y - 16z = c.$$

and

$$y = 2z + \frac{c-64}{8}$$

the equation of a line parallel to the side B C of the triangle.   The coordinates of the points of such a line indicate the composition of mixtures which will burn with production of the same amount of potassic carbonate.   The amount of potassic carbonate is constant for each parallel line, but changes from one line to another.   Now as they intersect the lines B D and D C, it is only necessary to ascertain the amounts of potassic carbonate corresponding to the points of one of these sides in order to know the amount of potassic carbonate formed by the combustion of a mixture represented by the coordinates of any point within the triangle.

Similar considerations lead to the equation :

$$y = \tfrac{1}{4}z + \frac{320-c}{16}$$

for mixtures which will burn with production of equal quantities of potassic sulphate.

This is the equation of a line parallel to the side D C. All these parallel lines intersect the line D B. If, then, we know the quantity of potassic sulphate corresponding to each point of D B, we shall likewise know the amount of this salt which any mixture, the composition of which is represented by the coordinates of one of the points of the triangle, can produce by its combustion. Now the powders, the composition of which is given by the coordinates of the points of B D produce by their combustion an amount of potassic sulphate which in molecules is directly expressed by the length of the corresponding abscissæ of the points.

Since x has been taken constant $=16$, the sum of the molecules of the potassium salts must always be $=8$, and as the points of the line B D represent only mixtures which burn with the production of two of these salts, potassic carbonate and sulphate, it is only necessary in order to know the respective quantities of each of these salts for a point F on B D, to subtract the value of the abscissa of F from 8 to obtain the molecules of potassic carbonate which would be produced by the combustion of a mixture the composition of which is given by the coordinates of F.

The coefficient of potassic disulphide in equation (XIII.) is $=-160+8y+12z$, from which we deduce the equation :

$$y = -\tfrac{3}{2}z + \frac{c+160}{8}$$

which is the equation of a line parallel to side B D. The points of such a line represent by their coordinates mixtures which will burn with the production of the same amount of potassic disulphide, which amount is constant for the same line, but changes from one to another. This amount is found for a mixture represented by the coordinates of a point P, if through P a line is drawn parallel to B D, and the abscissa of the point of intersection with the side D C is ascertained; half the length of this abscissa represents the number of molecules of potassic disulphide formed by the combustion of the mixture represented by point P.

For mixtures which are to burn with the evolution of the same quantity of carbonic acid we have :

$$-64 + 20y + 16z = c$$

or

$$y = -\tfrac{4}{5}z + \frac{c+64}{20}$$

an equation which represents a line parallel to G H, on which for two points y, z and y', z', five times the difference of the ordinates is equal to four times the difference of the abscissæ.

The line D V in our figure is parallel to G H. In order to find the amount of

carbonic acid which is developed by the combustion of a mixture the composition of which is represented by the coordinates of a point P, we have to draw through P a line parallel to D V or G H, and determine the length of the ordinate of the point of intersection with the side B C; this length is equal to the number of molecules of carbonic acid, because for all mixtures represented by the points of the side B C, the number of molecules of carbonic acid produced is equal to the number of atoms of carbon the mixtures contain.

We will now proceed to determine, by aid of the method just explained, the quantities of the products of combustion of a mixture the composition of which is represented by the coordinates of the point R on D V, $y=16$, $z=5$. A line drawn through R parallel to D C intersects D B in the point S; the abscissa of S$=3$, hence 3 mols. of potassic sulphate are produced.

A line drawn through R parallel to B C, cuts the side D B, in F; the abscissa of F$=4$; $8-4=4$; hence we obtain 4 mols. of potassic carbonate.

A line through R parallel to D B, intersects D C, in point U; the abscissa of U$=2$; $\frac{2}{2}=1$; hence 1 mol. of potassic disulphide is formed.

R is a point of D V, the ordinate of V, y, $=12$, hence we have 12 mols. of carbonic acid.

Nitrogen is for all mixtures a constant $=8N_2$, therefore the equation for the metamorphosis of a mixture, the composition of which is expressed by the coordinates of the point R is:

$$16KNO_3 + 16C + 5S = 4K_2CO_3 + 3K_2SO_4 + K_2S_2 + 12CO_2 + 8N_2$$

The great advantage of the geometrical construction of the coefficients of equation (XIII.) consists in this, that we can at once ascertain by an inspection of figure B C D, the influence of all possible variations of the quantities of carbon and sulphur in given mixtures, upon the proportions of the corresponding products of combustion.

Similar considerations enable us to find the quantities of gas and heat.

If we add the constant 8 for nitrogen to the number of molecules of carbonic acid determined as previously explained, we obtain the total number of gas molecules produced by the combustion of a mixture represented by the coordinates of a given point.

The heat generated is found by equation (X.).

For powders which shall produce by their combustion the same amount of heat, we have:

$$1 \cdot 92y = -z + \frac{1827154 - c}{8788}$$

for which we may adopt without serious error

$$2y = -z + \frac{1827154 - c}{8788} \quad \cdot \quad \cdot \quad \cdot \quad \cdot \quad \cdot \quad \cdot \quad \cdot \quad \text{(XVII.)}$$

This is the equation of a line perpendicular to the side B C. For an appropriate value of c it becomes :

$$2y = -z + 40$$

and then represents the line D W in the figure.

Mixtures, the composition of which can be represented by the points of such a line, will generate by their combustion very nearly the same amount of heat. A powder composed of $16KNO_3 + 20C$ corresponds to the point D, and one consisting of $16KNO_3 + 14 \cdot 4C + 11 \cdot 25S$ to the point W. The first generates according to equation (X.) 1,488,654, and the second 1,484,569 units of heat, two numbers which differ only by $0 \cdot 27$ per cent., and may therefore be considered identical for practical purposes.

A line drawn through the point R, perpendicular to the side B C, intersects the latter in the point $y = 13 \cdot 25$, $z = 10 \cdot 6$; hence two powders composed of

$$16KNO_3 + 16C + 5S$$
$$\text{and } 16KNO_3 + 13 \cdot 25C + 10 \cdot 6S$$
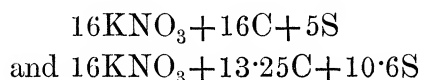
will generate by their combustion the same, or more correctly, nearly the same amount of heat.

Consequently, if we know the heat of combustion of all the mixtures represented by the coordinates of the points of the line B C, then we know likewise the heat of combustion of all the mixtures the composition of which is represented by *any* point within the triangle. And we arrive at the same conclusion with regard to the amount of gas which a mixture can produce, the composition of which is represented by any point inside the triangle B C D. According to equation (X.) the heat of combustion reaches its maximum when y and z assume their smallest values, and, on the other hand, when y and z are greatest the heat of combustion will be a minimum. Therefore, an inspection of the triangle B D C teaches that of all the infinite number of mixtures of saltpetre, carbon, and sulphur which can be transformed according to equation (XIII.), the one which is composed of

$$16KNO_3 + 8C + 8S$$
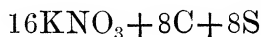
will produce by its combustion the greatest, and the one composed of

$$16KNO_3 + 24C + 16S$$
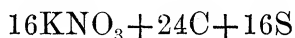
the smallest quantity of heat : the first is represented by point B, the second by point C of the figure.

Further, it follows from equation (IX.) that the first of the above mixtures will form the smallest, and the second the largest quantity of gas.

If then we place ourselves at the point B of line B C, to which corresponds the generation of the greatest quantity of heat and that of the smallest quantity of gas,

and move from B towards C, the amounts of heat produced by the mixtures represented by the coordinates of the several points will constantly decrease, and the volumes of gas increase, until the former reach in C their minimum, and the latter their maximum value.

We calculate for B and C

	Volume of gas.	Units of heat.
B . . .	32	1,621,450
C . . .	64	1,280,346

and between these numbers, 32 and 64 for the volume of the gas, and 1,280,346 and 1,621,450 for the units of heat, fluctuate the quantities of heat and gas which any possible mixture of 16 mols. of saltpetre with carbon and sulphur can produce, provided that these constituents, during combustion, transform themselves according to equation (XIII.). We will now show that the product, E, of the units of heat and the molecules of gas as given by equation (XI.), is greater for mixtures represented by points of line B C than for such as are represented by any other point within the triangle.

If we take, on the line D W, perpendicular to B C, the point $y=17$, $z=6$, then the mixture corresponding to this point and the one corresponding to point W will produce the same quantity of heat. The amount of gas generated by the mixture represented by point $y=17$, $z=6$, must be less than the quantity produced by the mixture corresponding to point W. Because, if we draw a line through $y=17$, $z=6$, parallel to D V, the point of intersection with B C will lie between W and V; but the further the point of intersection is away from W in the direction towards B the smaller the volumes of gas will be. Hence, the product of gas and heat for $y=17$, $z=6$ must be smaller than the one for point W, and the further we proceed from W towards D the smaller this product must be. But what holds good for the line D W also applies to every other perpendicular which can be drawn to B C.

Therefore the maximum value of the product of gas and heat must be produced by a mixture the composition of which is expressed by the coordinates of one of the points of the line B C.

If we represent the function on the right of the equation (XI.) by F(y, z), and the equation of the line B C (XIV.) by $\phi(y, z)=0$, then the differential equation

$$\frac{d\mathrm{F}}{dz}\cdot\frac{d\phi}{dy}-\frac{d\mathrm{F}}{dy}\cdot\frac{d\phi}{dz}=0$$

together with $\phi(y, z)=0$ give the values of y and z, for which E in equation (XI.) becomes a maximum. We find $y=38\cdot02$ and $z=23\cdot0$. Hence, a powder composed of

$$16KNO_3+38C+23S$$
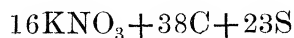
will by its complete combustion produce amounts of heat and gas the product of which will be the required maximum. But a mixture which shall transform itself according to equation (XIII.), can only contain per 16 mols. of saltpetre from 8 to 24 atoms of carbon, and from 8 to 16 atoms of sulphur. Hence, the product of the quantities of heat and gas will be a maximum for a powder composed of

$$16KNO_3 + 24C + 16S$$
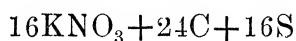
because according to the coefficients of equation (XI.) E will become greater and greater when y increases from 8 to 24, and z from 8 to 16, until it reaches its maximum value at a point $y=38$ and $z=23$, outside the triangle B C D.

For the purpose of calculating the values of E for different mixtures, we may simplify the coefficients and constant of equation (XI.), and write accordingly

$$10441 - 12{\cdot}1y^2 + 1208{\cdot}4y - 16yz + 994z - 5z^2 = E \quad . \quad . \quad . \quad \text{(XVIII.)}$$

E has been calculated by means of this equation for different values of y and z with the following results :—

$y=\ 8,$	$z=\ 8,$	$E = 25941{\cdot}8$
$y=10,$	$z=\ 9,$	$E = 28416$
$y=12,$	$z=10,$	$E = 30719{\cdot}4$
$y=14,$	$z=11,$	$E = 32852$
$y=16,$	$z=12,$	$E = 34813{\cdot}8$
$y=18,$	$z=13,$	$E = 36604{\cdot}8$
$y=20,$	$z=14,$	$E = 38225$
$y=22,$	$z=15,$	$E = 39674{\cdot}4$
$y=24,$	$z=16,$	$E = 40953{\cdot}0$

If, therefore, the carbon and the sulphur increase in different mixtures, the carbon by 2 atoms and the sulphur by 1 atom from

$$16KNO_3 + 8C + 8S$$

to

$$16KNO_3 + 24C + 16S$$
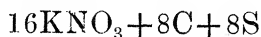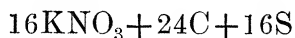
then parallel with this change of the carbon and sulphur, a regular increase of the product of heat and gas takes place, until for 24C and 16S it becomes a little more than one-and-a-half times as great as for 8C and 8S.

If saltpetre and sulphur remain constant, and the carbon alone changes, then also an increase of the carbon is followed by one of E.

$y=\ 8,$	$z=8,$	$E = 25941{\cdot}8$
$y=16,$	$z=8,$	$E = 32261{\cdot}8$
$y=18,$	$z=8,$	$E = 33599{\cdot}8$
$y=22,$	$z=8,$	$E = 35985{\cdot}8$

The energy of a powder of the composition :

$$16KNO_3 + 22C + 8S$$
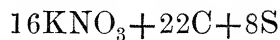
in about $\frac{2}{5}$ths greater than that of one containing :

$$16KNO_3 + 8C + 8S.$$
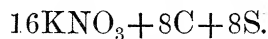
If saltpetre and carbon are constant, but the sulphur changes, we obtain the following values for E :—

$y = 14,$	$z = 4,$	$E = 27987 \cdot 0$
$y = 14,$	$z = 11,$	$E = 32852 \cdot 0$
$y = 16,$	$z = 6,$	$E = 30925 \cdot 8$
$y = 16,$	$z = 8,$	$E = 32261 \cdot 8$
$y = 16,$	$z = 12,$	$E = 34813 \cdot 8$
$y = 18,$	$z = 8,$	$E = 33599 \cdot 8$
$y = 18,$	$z = 13,$	$E = 36604 \cdot 8$
$y = 20,$	$z = 0,$	$E = 29769$
$y = 20,$	$z = 5,$	$E = 33014$
$y = 20,$	$z = 9,$	$E = 35430$
$y = 20,$	$z = 14,$	$E = 38225$
$y = 22,$	$z = 8,$	$E = 35985 \cdot 4$
$y = 22,$	$z = 15,$	$E = 39674 \cdot 4$

It follows from these examples that for a constant quantity of saltpetre, in varying mixtures of saltpetre, carbon, and sulphur, the relative energy of the mixtures increases with both the carbon and the sulphur, and reaches its maximum for 24 atoms of carbon and 16 atoms of sulphur, the highest amounts of these constituents which can exist in a powder according to equation (XIII.).

The difference of E for two mixtures of the same amount of saltpetre, but varying quantities of carbon and sulphur, becomes much smaller with equal weights of such mixtures. If, then, we multiply x, y, and z with their respective molecular or atomic weights, and divide E by the sum of the numbers so obtained, we find the relative energy, say E′, of equal weights of various mixtures.

The following table gives the value of E′ for mixtures which contain 16 mols. of KNO_3, y atoms of C, and z atoms of S.

$y = 8,$	$z = 8,$	$E' = 13 \cdot 18$
$y = 16,$	$z = 8,$	$E' = 15 \cdot 63$
$y = 18,$	$z = 8,$	$E' = 16 \cdot 09$
$y = 22,$	$z = 8$	$E' = 16 \cdot 84$

$$y=11, \qquad z= 6, \qquad E'=13\cdot91$$
$$y=13, \qquad z= 6, \qquad E'=14\cdot58$$
$$y=16, \qquad z= 6, \qquad E'=15\cdot46$$
$$y=21, \qquad z= 6, \qquad E'=16\cdot62$$

$$y=11, \qquad z= 6, \qquad E'=13\cdot91$$
$$y=11, \qquad z= 9\cdot5, \qquad E'=14\cdot41$$

$$y=14, \qquad z= 4, \qquad E'=14\cdot63$$
$$y=14, \qquad z= 8, \qquad E'=15\cdot11$$
$$y=14, \qquad z=11, \qquad E'=15\cdot38$$

$$y=16, \qquad z= 2\cdot66, \qquad E'=15\cdot11$$
$$y=16, \qquad z= 6, \qquad E'=15\cdot46$$
$$y=16, \qquad z= 8, \qquad E'=15\cdot63$$
$$y=16, \qquad z=12, \qquad E'=15\cdot88$$

$$y=18, \qquad z= 8, \qquad E'=16\cdot09$$
$$y=18, \qquad z=13, \qquad E'=16\cdot28$$

$$y=20, \qquad z= 0, \qquad E'=16\cdot03$$
$$y=20, \qquad z= 5, \qquad E'=16\cdot37$$
$$y=20, \qquad z= 9, \qquad E'=16\cdot52$$
$$y=20, \qquad z=14, \qquad E'=16\cdot59$$

$$y=21, \qquad z= 4, \qquad E'=16\cdot54$$
$$y=21, \qquad z= 6, \qquad E'=16\cdot62$$

$$y=22, \qquad z= 8, \qquad E'=16\cdot84$$
$$y=22, \qquad z=15, \qquad E'=16\cdot81$$

$$y=24, \qquad z=16, \qquad E'=16\cdot95$$

It follows from these numbers that E' becomes greater when y or z, or both simultaneously, increase, but proportionately less so than is the case with weights of mixtures which contain equal weights of saltpetre, viz., 16 mols.

The smallest value of E' is $13\cdot18$, the highest $16\cdot95$; hence the latter is about 28 per cent. greater.

The highest value of E, on the other hand, is more than 50 per cent. greater than the lowest. Further, it is apparent that for mixtures for which y and z assume high values the differences of E' become very small.

The powder

$$16KNO_3+14C+4S$$

differs from

$$16KNO_3+14C+11S$$
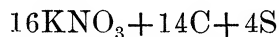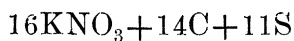
by 7 atoms of sulphur.

The two mixtures

$$16KNO_3 + 22C + 8S$$
$$\text{and } 16KNO_3 + 22C + 15S$$
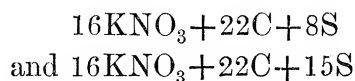
differ by the same amount of sulphur.

The two former show, for E′, the difference 0·75, the latter only 0·03; indeed, many of the various mixtures for which y and z have high values, give, when equal weights are considered, almost the same number for E′.

If we draw a line through the triangle B C D (see fig. 1), from the point $y=22$, $z=8$ to the point $y=8$, $z=8$, it will be observed that for mixtures represented by the coordinates of the points on the right-hand side of this line, the value of E′ only increases very little if the sulphur is increased beyond 8 atoms and the carbon kept constant. This circumstance is of great practical importance. The analyses of military and sporting powders known to me, all give for 16 mols. of saltpetre an amount of sulphur which varies between 5·5 and 8·7 atoms. There would be very little, if any, gain in energy if, for 16 mols. of saltpetre, more than about 8 atoms of sulphur were introduced into the powder; especially would this be the case with mixtures in which for 16 mols. of saltpetre more than 16 atoms of carbon are present.

E′ obtains its maximum value, 16·95, when the powder contains:

$$16KNO_3 + 24C + 16S.$$
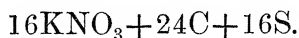
Such a large amount of sulphur does not, according to the foregoing remarks, contribute much to the value of E′, whereas, on the other hand, it must be very detrimental to the metal of the ordnance. For the mixture

$$16KNO_3 + 22C + 8S$$
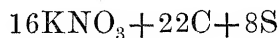
we have E′=16·84, hence, only 0·67 per cent. less than for $16KNO_3+24C+16S$.

If carbon and sulphur undergo a further diminution, the decrease of E′ becomes more rapid; for

$$16KNO_3 + 21C + 4S$$
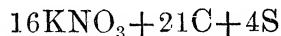
E′=16·54. If, therefore, we had to choose between the two mixtures

$$16KNO_3 + 24C + 16S$$
$$\text{and }   16KNO_3 + 22C + 8S$$
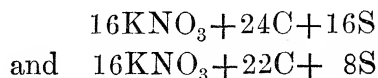
for the composition of a service powder the second would recommend itself as the more suitable.

We will now compare the composition and energy of the ordinary gunpowders with the results of the foregoing theoretical considerations.

The composition of the powders of Waltham Abbey can be represented by the symbols:

$$16KNO_3 + 21·18C + 6·63S$$
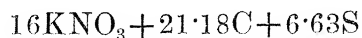
which corresponds nearly to 75 parts of saltpetre, 10 parts of sulphur, and 15 parts of charcoal.

About these numbers fluctuate the compositions of the service powders of most nations.

Composition of gunpowders.

	Saltpetre.	Charcoal.	Sulphur.
England	75	15	10
Sweden	75	15	10
Russia	75	15	10
Prussia	74	16	10
Saxony	74	16	10
United States . . .	76	14	10
Austria	75·5	14·5	10

If, therefore, the composition of a gunpowder is required which shall possess nearly the greatest energy, and at the same time contain the smallest amount of sulphur compatible with this condition, an experience extending over 500 years has selected a mixture which contains saltpetre, carbon, and sulphur nearly in the theoretical proportions.

Composition of powders of Waltham Abbey. . $16KNO_3 + 21·18C + 6·63S$

Theoretical composition. . . . . $16KNO_3 + 22C + 8S$.

We concluded from KAROLYI's experiments that the most inflammable and combustible mixture is represented by

$$16KNO_3 + 13C + 5S$$
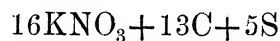
BUNSEN and SCHISCHKOFF found in their sporting powder

$$16KNO_3 + 13·3C + 6·3S$$
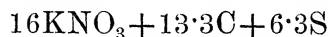
The value of E′ for the proportions of saltpetre, carbon, and sulphur exhibited in the powders of Waltham Abbey is very nearly 16·62; for BUNSEN and SCHISCHKOFF's sporting powder 14·58. Consequently 12·2 per cent. of the energy of the English service powder has been sacrificed in order to obtain the greater combustibility of the sporting powder.

According to composition, the service powders of France, Spain, Belgium, and Würtemberg are intermediate between the two powders just considered. They fluctuate about the proportions required by the symbols

$$16KNO_3 + 16C + 8S$$
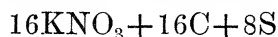
E′ for these powders equals 15·63, or about 6 per cent. less than for the English; but they will, probably, be more inflammable and combustible than the latter.

It is worthy of notice that the points which represent, by their coordinates, the proportions of saltpetre, carbon, and sulphur in the gunpowders considered in this paper, are situated between two ordinates on our triangle B C D, for which respectively z assumes the values 5·5 and 8·7. The powders of Waltham Abbey, and BUNSEN and SCHISCHKOFF'S sporting powder contain per 16 mols. of saltpetre, nearly the same amount of sulphur ; the former are represented by a point near the line D C, the latter by one near the line B D, of our figure B C D.

Summary of the main results.

1. The mean composition of the powders of Waltham Abbey can be represented by the symbols :

$$16KNO_3 + 21·18C + 6·63S$$
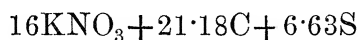
A powder of this composition is transformed in NOBLE and ABEL'S apparatus according to the equation :

$$16KNO_3 + 21C + 5S = 5K_2CO_3 + K_2SO_4 + 2K_2S_2 + 13CO_2 + 3CO + 8N_2 \quad . \quad \text{(II.)}$$
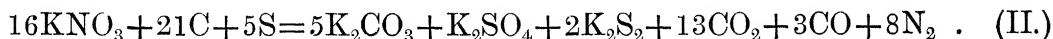
The residue of the sulphur, 1·63 atoms, unites partly with hydrogen, partly with the iron of the apparatus.

2. The ordinary service and sporting powders contain for every 16 mols. of saltpetre from 13 to 22 atoms of carbon, and from 5·5 to 8·7 atoms of sulphur.

3. A powder composed of *pure* carbon, saltpetre, and sulphur furnishes by its *complete* combustion potassic carbonate, potassic sulphate, potassic *disulphide*, carbonic acid, carbonic oxide, and nitrogen, as chief products.

4. An increase of pressure appears, *cæteris paribus*, to diminish the amount of carbonic oxide, and, in consequence, according to equation (VIII.), to increase the quantities of potassic carbonate, potassic disulphide, and carbonic acid, and diminish that of potassic sulphate. These fluctuations depending on pressure are, however, *very small*. In NOBLE and ABEL'S Experiment No. 38, the pressure amounted to 18·6 tons, in Experiment No. 77 to 31·4 tons on the square inch, Experiment No. 38 gave for every 16 mols. of decomposed saltpetre 3·36 mols. of carbonic oxide, and Experiment No. 77, 2·9 mols. of this gas, or, for a difference of 12·8 tons in pressure, one of 0·46 mol. of carbonic oxide. A diminution of 0·5 mol. of carbonic oxide corresponds to one of 0·143 mol. in the amount of potassic sulphate, and an increase of 0·071 mol. in that of the potassic carbonate and disulphide, and 0·428 mol. in the quantity of carbonic acid. These fluctuations are probably not caused directly by the pressure, but by the differences in the rate of cooling after explosion.

5. The combustion of gunpowder takes place in two stages, one succeeding the other.

(*a.*) A process of oxidation during which potassic sulphate, carbonate, carbonic acid

and nitrogen, and, *perhaps,* some carbonic oxide, but no potassic disulphide, are produced.

(*b.*) A process of reduction during which carbon and sulphur left free at the end of the first stage react with some of the products formed during that stage; the free carbon reducing potassic sulphate, with formation of potassic disulphide, potassic carbonate, and carbonic acid; the free sulphur decomposing potassic carbonate with the production of potassic disulphide, potassic sulphate, and carbonic acid [equations (V.) and (VI.)].

6. The first stage of the combustion, the explosion proper, takes place with powders of various composition according to equation :

$$10KNO_3 + 8C + 3S = 2K_2CO_3 + 3K_2SO_4 + 6CO_2 + 5N_2 \quad . \quad . \quad . \quad \text{(III.)}$$

But as some carbonic oxide is probably produced at the same time, the following will more correctly represent the reactions.

$$16KNO_3 + 13C + 5S = 3K_2CO_3 + 5K_2SO_4 + 9CO_2 + CO + 8N_2 \quad . \quad . \quad \text{(IV.)}$$

The constituents of the powder and the products of combustion are, according to (IV.), nearly in the same ratios as according to (III.).

7. The oxygen in the potassic carbonate stands to the oxygen in the potassic sulphate and carbonic acid, respectively, in equation (III.), in the most simple ratios which can exist, if these substances are to be produced by the combustion of a mixture of saltpetre, carbon, and sulphur. In other words, equation (III.) represents the most simple distribution of the oxygen of the decomposed saltpetre amongst the products of the first stage of the combustion. And because the products are, according to equation (IV.), nearly in the same proportions they assume to (III.), it follows that the distribution of the oxygen between potassic sulphate, carbonate, and carbonic acid, according to (IV.), nearly corresponds to the most simple possible distribution.

8. If the greatest possible amount of heat is to be evolved by the combustion of a mixture of saltpetre, carbon, and sulphur, and if at the same time potassic sulphate, carbonate, and carbonic acid are to be formed in such proportions that the heat of formation of one of them shall stand to the heat of formation of each of the others in the most simple ratio, then the combustion must take place according to equation (IV.).

The heat produced by the formation of 3 mols. of potassic carbonate stands to that produced by the formation of 5 mols. of potassic sulphate and 9 mols. of carbonic acid respectively, as

$$1 : 2 \cdot 05 : 1 \cdot 04$$

9. The ordinary gunpowders contain more carbon and sulphur than is required by equation (IV.).

This excess of carbon and sulphur is left free at the end of the first stage of the combustion.

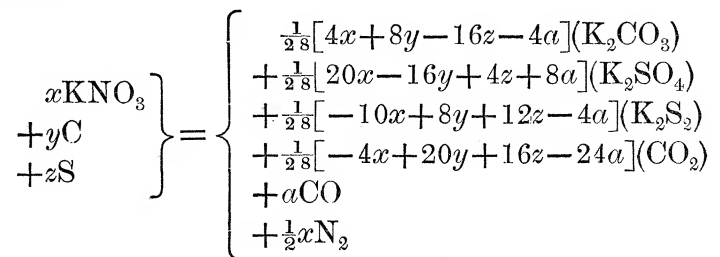The free carbon now acts according to equation:

$$4K_2SO_4 + 7C = 2K_2CO_3 + 2K_2S_2 + 5CO_2 \quad . \quad . \quad . \quad . \quad . \quad \text{(VI.)}$$
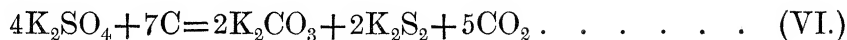
the free sulphur upon the potassic carbonate as follows:

$$4K_2CO_3 + 7S = K_2SO_4 + 3K_2S_2 + 4CO_2 \quad . \quad . \quad . \quad . \quad . \quad \text{(V.)}$$

and both united form the second stage of the combustion. These reactions are endo-thermic; heat is not evolved but consumed; they are not of an explosive nature, and in practice are probably seldom complete.

The reactions of this second stage increase the volume of the gas formed during the first stage of the combustion and diminish the temperature of the products. A portion of the carbonic oxide is formed during the second stage by the action of free carbon or potassic disulphide upon carbonic acid.

10. The reactions represented by equations (III.), (IV.), (V.), and (VI.) can be expressed by one equation. If x, y, and z are positive numbers, and a indicates how many molecules of carbonic oxide are formed by the combustion of a weight of powder, containing x molecules of saltpetre, y atoms of carbon, and z atoms of sulphur, the following will be the general equation representing the complete chemical meta-morphosis of powder.

$$\left.\begin{array}{c} x KNO_3 \\ +yC \\ +zS \end{array}\right\} = \left\{\begin{array}{l} \frac{1}{28}[4x+8y-16z-4a](K_2CO_3) \\ +\frac{1}{28}[20x-16y+4z+8a](K_2SO_4) \\ +\frac{1}{28}[-10x+8y+12z-4a](K_2S_2) \\ +\frac{1}{28}[-4x+20y+16z-24a](CO_2) \\ +aCO \\ +\frac{1}{2}xN_2 \end{array}\right.$$

11. If $x=16$, and $a=0$, the volume of the gas, (V.), generated by complete combustion is nearly
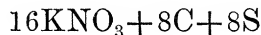
$$= \frac{160+20y+16z}{14} . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad \text{(IX.)}$$

and the units of heat, W,

$$= 1000[1827 \cdot 154 - 16 \cdot 925y - 8 \cdot 788z] \quad . \quad . \quad . \quad . \quad . \quad \text{(X.)}$$

y signifies in these equations the number of carbon and z that of the sulphur atoms in a weight of powder containing 16 mols. of saltpetre.

The volume of gas becomes greater and the heat of combustion diminishes with an increase of y and z, and *vice versâ*.

The mixture containing :

$$16KNO_3 + 8C + 8S$$

produces the greatest amount of heat and the smallest quantity of gas, and the mixture represented by the symbols :

$$16KNO_3 + 24C + 16S$$
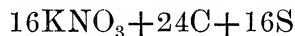
the largest volume of gas and the smallest quantity of heat.

12. The product E obtained by the multiplication of V and W (equations IX. and X.) will approximately represent the relative energies of mixtures of various composition.

The mixture represented by the symbols

$$16KNO_3 + 24C + 16S$$
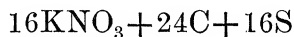
is of all the infinite number of mixtures which can transform themselves according to equation (XIII.) the one for which E assumes the greatest value. Hence, a powder of this composition possesses the greatest energy.

13. If a mixture of saltpetre, carbon, and sulphur were required which shall possess nearly the greatest energy, and at the same time contain the smallest amounts of carbon and sulphur compatible with this condition, theory would point to the mixture :

$$16KNO_3 + 22C + 8S$$
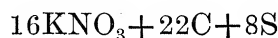
The service powders of most nations fluctuate about :

$$16KNO_3 + 21 \cdot 2C + 6 \cdot 6S$$
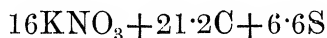
14. Gunpowder, however, does not contain pure carbon, but besides this element hydrogen and oxygen as constituents of the charcoal.

The oxygen is eliminated with a portion of the hydrogen in the form of water, the remainder of the hydrogen remains either free or unites with carbon, sulphur, and nitrogen respectively, producing sulphuretted hydrogen, ammonia, and marsh gas.
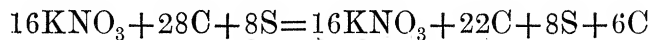
These secondary products only amount from 1 to 2 per cent. of the powders.

15. Mining powders contain much more carbon than is required according to equation (XIII.). In consequence, the oxygen of the charcoal is not eliminated during the combustion of these powders with hydrogen, as water, but in combination with carbon as carbonic oxide and carbonic acid.

The hydrogen thus left free causes the formation of a comparatively large proportion of sulphuretted hydrogen and marsh gas. The potassic sulphocyanate is also produced in quantities much larger than those formed by the service powders on account of the carbon left free at the end of the combustion. If we neglect these secondary products, then the combustion of mining powder may be represented by the simple equation :
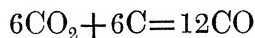
$$16KNO_3 + 28C + 8S = 4K_2CO_3 + 4K_2S_2 + 12CO_2 + 12CO + 8N_2$$
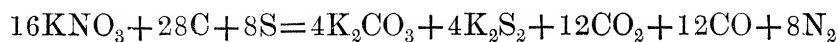
The reactions can also be represented as follows :

$$16KNO_3 + 28C + 8S = 16KNO_3 + 22C + 8S + 6C$$

16 mols. of saltpetre, 22 atoms of carbon, and 8 atoms of sulphur transform themselves according to (XIII.) as follows:

$$16KNO_3 + 22C + 8S = 4K_2CO_3 + 4K_2S_2 + 18CO_2 + 8N_2$$
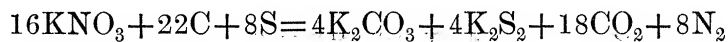
If, now, **6** atoms of carbon act on 6 mols. of CO_2 we obtain

$$6CO_2 + 6C = 12CO$$

In this manner we can conceive the combustion of a mining powder to take place according to the same equations which apply to ordinary gunpowder, and that the excess of carbon in the mining powder causes, subsequently, the reduction of a portion of the carbonic acid to carbonic oxide.